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# SOIL SCIENCE

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## SOIL SCIENCE



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## NITRATE ACCUMULATION UNDER THE STRAW MULCH

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In a previous paper by the senior author (1) reporting data on studies on nitrate accumulation in soil under a straw mulch, a negative relation between moisture and nitrate accumulation was suggested. Little nitrate nitrogen accumulated regularly in the mulched soil, and only as the moisture was lessened in drier weather did nitrates accumulate. Further study has been conducted in the hope of isolating the factors and conditions connected with moisture that were responsible for the small amounts of nitrates under the mulch.

### CONDITIONS INFLUENCING NITRIFICATION

The literature on nitrification directs attention to the following factors; influence of temperature (10, 11, 16); effect of moisture (4, 7, 10, 14, 15, 25); influence of mechanical composition (14, 16, 17, 19, 23), of aeration (2, 7, 10, 18), of air-drying (3, 9, 10, 11, 13, 20), of acidity (5, 23, 24), and of organic matter in the soil (17, 21, 22). In this study the acidity and organic matter as significant factors were eliminated by nitrate studies on the same soil mulched and unmulched in the greenhouse. Aeration was controlled by compressed air, and the effect of air-drying was determined by comparing the soils air-dried when put into the greenhouse with those brought in without loss of moisture. In this way it was possible to isolate the factor or factors of this group connected with the depression of nitrate accumulation under the straw-mulched soil as compared with the soil unmulched.

### NATURE OF SOIL USED

The soil used, similar to that of the previous experiment, is a brown silt loam of glacial origin with a fine friable structure, about eight inches deep and underlain by a rather tight, mottled, silty clay loam. Three plots, with treatments given in table 1, constituted the series used in the study. In the early trials all three plots were used, but as it was evident that the lighter mulch had effects similar to those of the heavier application but to a lesser degree, most of the data from the plot with the 2-ton mulch are omitted here, and no data were taken on this soil in the latter part of the study.

The total nitrogen in the surface soil of these plots<sup>1</sup> varied from 2223 pounds

<sup>1</sup> The total nitrogen determinations were made according to the method modified for nitrates, salicylic acid and sodium thiosulfate being used.

per 2 million in plot 6, to 2278 pounds in plot 5—a range within the limit of error of determinations, and a difference too insignificant to account for differences in nitrate accumulation. In the spring after the mulch had been removed and the soil had become dry enough to plow (April 17, 1923), these plots contained the amounts of moisture and nitrate shown in table 2.

According to the colorimetric hydrogen-ion determinations, made by following the method suggested by Gillespie (8), these soils have the following degree of acidity expressed as pH:

Plot 5.....	pH 5.8
Plot 6.....	5.6
Plot 7.....	5.2

TABLE 1  
*Treatment of soils*

PLOT NUMBER	SPRING TREATMENT	SUMMER AND WINTER TREATMENT
5	Mulch of 1922 removed, plowed and harrowed, 6 tons straw mulch applied April 24, 1923	Weeds pulled, no crop, no cultivation, mulch undisturbed
6	Mulch of 1922 removed, plowed and harrowed, 2 tons straw mulch applied	Weeds pulled, no crop, no cultivation, mulch undisturbed
7	Plowed and harrowed as were nos. 5 and 6, April 17, 1923	Surface scraped, no crop

TABLE 2  
*Moisture and nitrate nitrogen in soils at outset*

PLOT NUMBER	TREATMENT	WATER-FREE SOIL	WATER LOSS	WATER LOSS	NITROGEN AS NITRATE
		gm.	gm.	per cent	pounds per 2 million
5	Mulched 6 tons	86.33	13.66	15.82	13.7
6	Mulched 2 tons	84.41	15.58	18.46	14.5
7	Unmulched	84.68	15.32	18.09	10.4

Using the Comber (6) test for soil acidity, these plots showed an order of arrangement similar to that above, giving an appreciably lesser degree of acidity with mulch application.

So far as the "lime need" in terms of soluble iron, and the degree of acidity are concerned—if they are large enough to be of influence on nitrification—they would be expected to favor nitrification in the mulched plot rather than hinder it, since this plot has a lower hydrogen-ion concentration, and a lower "lime need" than the unmulched plot, both conditions favoring nitrate production. Apparently no condition innate to the soil was responsible. According to these suggestions, the depressing effect by the mulch must have come with the mulch, and was probably only temporary.

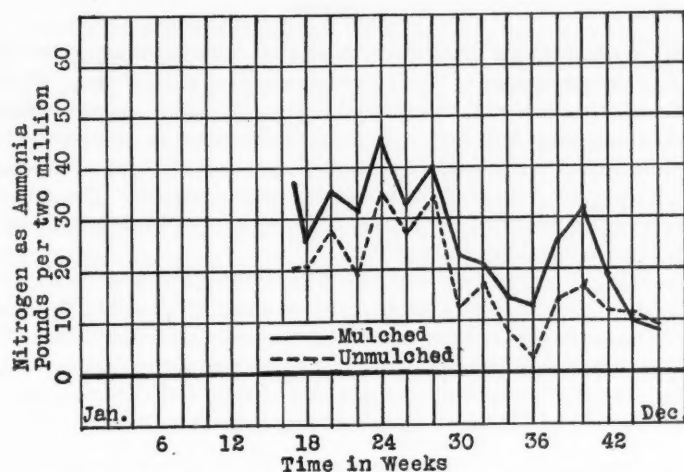


FIG. 1. AMMONIA ACCUMULATION IN STRAW MULCHED AND UNMULCHED SOILS (MAY TO DECEMBER)

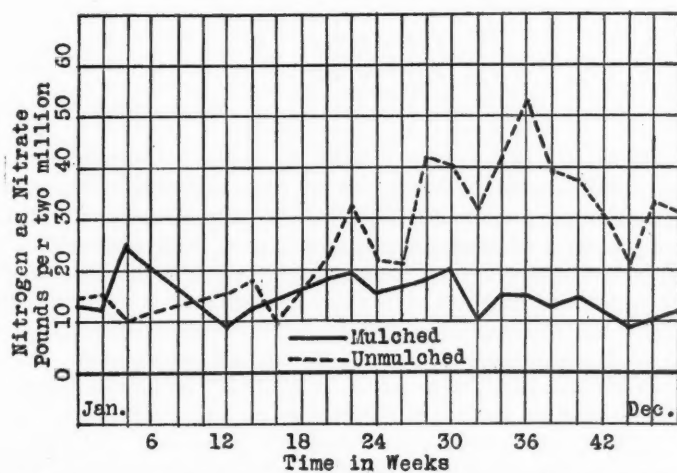


FIG. 2. NITROGEN AS NITRATE IN STRAW MULCHED AND UNMULCHED SOILS (JANUARY TO DECEMBER)

## FIELD STUDIES

Every 2 weeks nitrate determinations were made in triplicate on the field soils on composite samples of twelve borings per plot of 15 by 40 feet. To test whether nitrogen was being transformed in the soil, regular ammonia determinations were made from early May through the season, in addition to those for nitrates made during most of the year.<sup>2</sup> These were all based on moisture-free soil, and careful study of the moisture content was made. The data for the ammonia are presented as graphs in figure 1, those for nitrates in figure 2, and those for soil moisture in figure 3.

It is evident that the supply of ammonia under the mulch is not so low as to limit nitrification, since that in the mulched soil giving little nitrification is consistently higher than that in the unmulched where nitrates accumulated. The ammonia content and the nitrate content show no consistent relation, indicating that the conditions inhibiting nitrate accumulation under the mulch do not accomplish it by inhibiting ammonia production. It is evident from the

TABLE 3  
*Average temperatures*

PLOT	TREATMENT	TEMPERATURE
		°C.
5	Mulched 6 tons	24.6
6	Mulched 2 tons	25.5
7	No mulch	27.8

graphs in figure 3 that under the mulch the moisture is regularly higher<sup>4</sup> that in plot 5 being, as an average, 2.5 per cent higher than that in plot 7. There is further, as previous data have shown, a suggestion of inverse relation between moisture and nitrate accumulation in plot 5 under the mulch. The variations in moisture in many cases, however, were so small as compared to nitrate fluctuations, that this can scarcely be considered as the factor solely responsible for the depressing effect of the mulch on nitrate accumulation.

Increased moisture under the mulch gave lower soil temperatures. Data on temperatures recorded by thermometers at depths of 3 inches were usually the same on the mulched and unmulched plots in the early part of the day, or after a rain, but differed widely at 5 o'clock in the afternoon. The averages of weekly temperatures for daily readings at this time during June, July, August and September are given in table 3. The data emphasize the importance of the higher moisture under the mulch as a means of keeping the soil from warming as much during the day.

<sup>2</sup> Nitrate determinations were made on oven-dried samples. These were extracted with 0.0625*N* hydrochloric acid, the extract made alkaline, boiled to expel the ammonia, the volume replaced, De Varda's metal added, and distilled into standard acid.

Ammonia was determined by distilling 100 gm. of soil with magnesium oxide by means of steam and air.



While the field studies were being made, physical differences in the mulched and unmulched soils were apparent. With equal proportions of moisture in both soils, that from beneath the mulch was plastic, sticky, and of poor tilth, but the unmulched soil worked well. The former seemed more solid, more run together, and of much poorer tilth.

The data and observations pointed out that temperature differences in the two soils were not wholly responsible for the differences in nitrate accumulation; that the greater accumulation of ammonia under the mulch suggested poor nitrification but not poor ammonification; and that a poor physical condition of the soil resulted under the mulch carrying higher moisture.

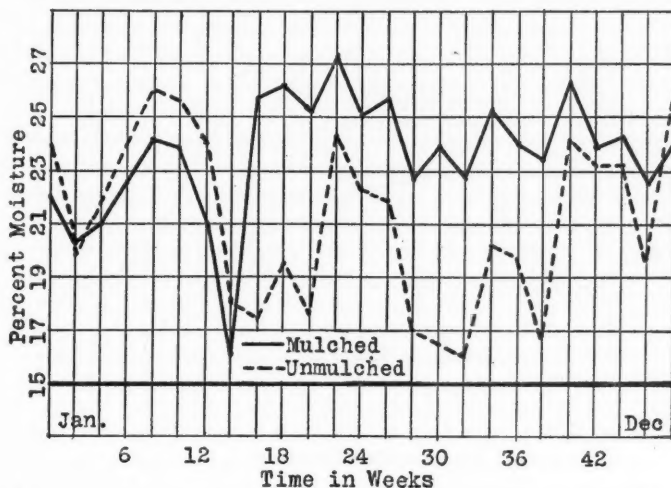


FIG. 3. MOISTURE IN STRAW MULCHED AND UNMULCHED SOILS (JANUARY TO DECEMBER)

#### POT EXPERIMENTS

As a result of the suggestions given in the data, some of the soils from the unmulched and the heavily mulched plots were brought into the greenhouse for a careful study of the possible causes of the low nitrate under the mulch. The unmulched soil in the field had an average moisture content for the previous summer seasons of 19 per cent, and the heavily mulched, 25 per cent. These figures were adopted as "normal" for these soils during the experiment. The soils were mixed by sifting, were put into 1-gallon jars, and moisture was maintained as near normal as possible. Part was thoroughly air-dried, and remoistened to test the effect of a single air-drying treatment on the nitrate accumulation; the rest was used with as little moisture loss as possible. At the outset these soils contained 15.9 pounds and 26 pounds nitrogen as nitrate,

per 2 million pounds of soil for the mulched and unmulched plots respectively. The following treatments were used in duplicate pots.

1. Fresh soil, check.
2. Fresh soil, ammonium sulfate.<sup>3</sup>
3. Soil air-dried, remoistened to normal moisture.
4. Soil air-dried, ammonium sulfate, remoistened to normal moisture.
5. Soil air-dried, remoistened to 25 per cent when normal was 19 or vice versa.
6. Soil air-dried, remoistened to 25 per cent when normal was 19 or vice versa, and previously unmulched soil mulched,<sup>4</sup> previously mulched soil left unmulched.

Nitrates were determined at the time the pots were set up, and then again at intervals of 6, 10, and 17 weeks to determine the accumulation of nitrogen

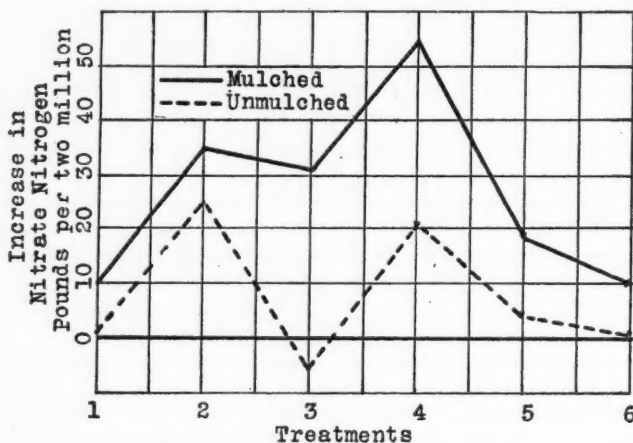


FIG. 4. INCREASE IN NITRATE NITROGEN IN STRAW MULCHED AND UNMULCHED SOILS IN POTS

Treatments

1. Fresh soil, check.
2. Fresh soil, ammonium sulfate.
3. Soil air-dried, remoistened to normal moisture.
4. Soil air-dried, remoistened to normal moisture, ammonium sulfate.
5. Soil air-dried, remoistened to 25 per cent, when normal was 19 per cent or vice versa.
6. Soil air-dried, remoistened to 25 per cent, when normal was 19 per cent or vice versa, and previously unmulched soil mulched, previously mulched soil left unmulched.

as nitrate under these conditions. The gains in nitrate nitrogen during the 17 weeks for the treatments on these two soils are shown in figure 4.

The general outstanding feature of these results is the marked difference in

<sup>3</sup> Ammonium sulfate was applied in solution at the rate of 3 mgm. of nitrogen per 100 gm. of soil.

<sup>4</sup> Straw was applied at the rate of 25 gm. per pot about 7 inches in diameter.

response in nitrate production by the soils from the mulched and unmulched plots. In the soil from the mulched plot, nitrate accumulation was greater under every treatment, indicating that this soil, put under different treatments, had even greater nitrate-producing power than the soil not mulched. Especially significant are the facts (a) that drying the mulched soil but once gave an increase in nitrate almost as large as that given by adding ammonium sulfate without drying; and (b) that air-drying and holding the moisture at 19 per cent, instead of the normal 25 per cent, also gave significant nitrate accumulation. In the unmulched soil the addition of ammonium sulfate was the only treatment that gave significant nitrate increases in the pots during the 17 weeks.

A marked difference in physical condition persisted in these soils, even after a single air-drying treatment at the outset. These differences are shown in plate 1. The soil under the mulch seldom froze at this latitude, consequently freezing and thawing as factors in maintaining good structure were little active. Alternate wetting and drying were also less significant in structural improvement, since the mulch prohibited, to no small extent, the loss of water;<sup>5</sup> nor was a new supply of air often being drawn into the soil, following the water removal by evaporation, which fact may be of great importance in explaining the irregularity in the accumulation of nitrates under the mulch. It may have been the beneficial effects in respect to structure and aeration that contributed to the marked improvement in nitrate accumulation in the mulched soil following a single air-drying.

#### AERATION STUDIES

As a result of the correlation between improved physical condition and increased nitrates in the mulched soil after air-drying, and to learn whether possibly the mulch was holding down nitrification through poor aeration caused by the high moisture and bad physical condition, the soils were put into tubes about two inches in diameter and eight inches deep through which air could be forced. Air was forced first through water to prevent drying of the soil and then through each tube separately, sometimes through the soil from the top downward and then from the bottom upward. The tubes were filled with the equivalent of 320 gm. oven-dry soil, a series each from the mulched and unmulched plots, and given the various treatments together with daily aeration for 45 days. The results in nitrate increase are shown in figure 5. The initial content of nitrate nitrogen for the mulched soil was 15.9 pounds per acre when fresh, and 9.8 pounds when dried; and for the unmulched soil it was 26.0 pounds when fresh, and 31.1 pounds when dried.

The outstanding result of this trial is the discovery of the influence of aeration in increasing the nitrate formed in both soils, whether mulched or

<sup>5</sup> For every gram of water lost from the unmulched soil there was a loss of but 0.4 gm. from the mulched soil. The mulched soil, air-dried, remoistened, and left unmulched, lost 13.4 per cent more water than the same treatment without air-drying.

unmulched, but especially in the former. This suggests that the deficiency in aeration may have been a factor responsible for the low nitrate accumulation in the mulched soil. The most significant increase resulted in the mulched soil, which was air-dried, brought again to its "normal" or high moisture content of 25 per cent, and then aerated. In this case the increase in nitrate nitrogen was 97.1 mgm. in 320 gm. dry soil in the period of 17 weeks. This suggests that aeration of this soil helps nitrate accumulation, but that this effect is much greater when the soil is first dried, restored to its moisture, and then aerated.

Since aeration gave marked results in connection with these soils, especially with the higher moisture content and after air-drying, another series of tubes

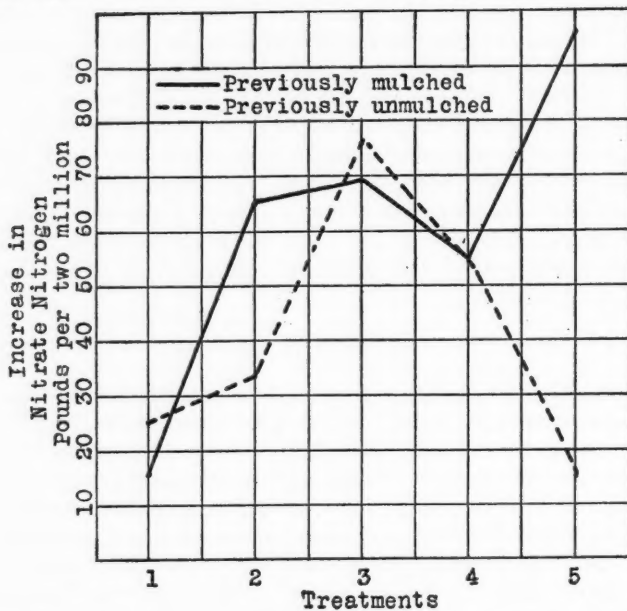


FIG. 5. INCREASE IN NITRATE NITROGEN IN SOILS IN AERATION TUBES (FIRST TRIAL)

*Treatments*

1. Soil from field, not aerated.
2. Soil from field, aerated.
3. Soil from field, aerated, ammonium sulfate.
4. Soil from field, not aerated, ammonium sulfate.
5. Soil air-dried, normal moisture, aerated.

was set up as before so that the effect of drying the soil, and the effect of raising the moisture content of the unmulched soil from 19 per cent (average in this plot) to 25 per cent (average in the field for the mulched plot), and of reducing it in the mulched soil from 25 per cent (average in this plot) to 19 per cent



(average in the field for the unmulched plot) might be noted. This test was run for 45 days during the winter. Although it did not give the gross increases as did the previous test, it gave differences comparable for treatments (fig. 6).

As in the previous test, aeration had a significant influence: it raised the nitrate content of the soil from the mulched plot to that in the unmulched soil, and gave the greatest increase in the soil previously mulched, but air-dried, remoistened and aerated.

That the moisture in connection with the physical condition is significant in holding down nitrate accumulation under the mulch is shown by three things; (a) the low nitrate content that occurred in the unmulched soil when the mois-

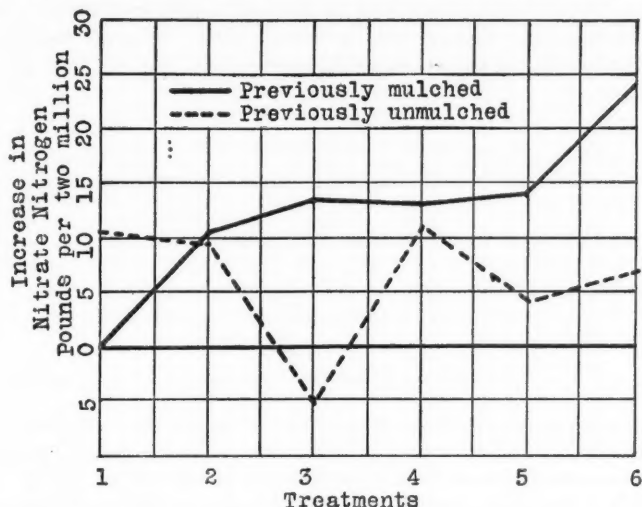


FIG. 6. INCREASE IN NITRATE NITROGEN IN SOILS IN AERATION TUBES (SECOND TRIAL)

*Treatments*

1. Soil from field, not aerated.
2. Soil from field, aerated.
3. Soil from field, moisture changed to 25 per cent when normal was 19 per cent or vice versa, not aerated.
4. Soil from field, moisture changed as in treatment 3, aerated.
5. Soil air-dried, normal moisture, not aerated.
6. Soil air-dried, normal moisture, aerated.

ture was raised to that of the mulched soil (25 per cent), (b) the significant nitrate increase in the previously mulched soil without aeration when its moisture was reduced, and (c) the nitrate increase when the previously mulched soil was merely dried and restored to its original moisture. The previously mulched soil gave especially high nitrates when in addition to the last treatment it was also aerated. -

The marked responses by these soils under the above condition suggest that mulching raised the moisture content of the soil and brought on a physical condition that slowed down nitrate accumulation. Forcibly aerating the soil, lowering its moisture, or drying it once to alter its physical condition increased the nitrate accumulation very markedly. It is well to remember that this soil had been under a straw mulch of about six tons per acre for almost four years, with the mulch removed in the spring only long enough to permit drying and plowing of the plot. When the mulch was removed and this soil plowed it showed poorer granulation and, in general, poorer tilth. The regularly high moisture content as a result of the cover and the failure of the mulched plot to undergo alternate wetting and drying, or alternate freezing and thawing—all of which provoke bad structure—may be responsible in no small measure for the differences in the nitrate accumulation between this soil and that left unmulched.

TABLE 4  
*Average of temperature readings*

	PREVIOUSLY MULCHED (FROM PLOT 5)				PREVIOUSLY UNMULCHED (FROM PLOT 7)			
	Unmulched		Mulched		Unmulched		Mulched	
Depth (inches).....	0	3	0	3	0	3	0	3
Temperature, °C.....	22°	20°	21°	21°	22°	21°	22°	22°

#### SOILS IN GREENHOUSE FLATS

The next step in the study consisted in reversing the conditions in the mulched and unmulched soils by bringing each of these soils into flats in the greenhouse, and giving each the treatment of a mulch and no mulch. Four flats, each 2 feet square and 1 foot deep were used, two with the soil from the previously unmulched plot and two from the mulched plot. One of each pair was given a straw mulch similar to that in the field and the other of the pair was left unmulched. In the field, the mulched plot commonly had a much lower temperature than the soil unmulched. In the greenhouse this was obviated, since the temperature records on these flats over the period of 29 days (table 4) show the average of readings about the same on all four flats, or no difference in favor of either the presence or absence of the mulch. Nitrate determinations were made on the flats at intervals of 5, 10, and 17 weeks with the results given in table 5.

The data show clearly the effect of removing the mulch as a means of increasing the nitrates, and the effect of adding the mulch as a means of depressing their accumulation. As bringing the soil into the greenhouse represents a different temperature condition and a different rate of moisture loss, some irregularities may have been caused by these. The soil from the unmulched plot never increased its total supply of nitrates whether mulched or unmulched; on the other hand, a significant decrease in nitrate nitrogen resulted when the mulch was applied and left for 17 weeks.

Here again the mulched soils, whether previously mulched or unmulched in the field, had the lower nitrates and also the higher constant moisture. The soils in all cases were brought up to the same moisture twice weekly. The soil having a mulch in the field lost 2.55 pounds of water when unmulched in the greenhouse, as compared to 1 pound when mulched. The soil not mulched in the field lost 2.39 pounds as compared to 1 pound for the above respective treatments in the greenhouse.

TABLE 5  
*Nitrate accumulation in soil as a result of mulching or removing mulch*  
(Pounds nitrate nitrogen per 2 million water-free soil)

FLAT NUMBER	TREATMENT	START	AFTER 5 WEEKS	GAIN	AFTER 10 WEEKS	GAIN	AFTER 17 WEEKS	GAIN
<i>Soil previously mulched (plot 5)</i>								
1	No mulch	10.97	15.24	4.27	21.63	10.66	19.54	8.57
2	Mulch	10.97	15.08	4.11	13.42	2.45	12.03	2.06
<i>Soil previously unmulched (plot 7)</i>								
3	No mulch	34.78	24.99	-9.79	30.53	-4.25	25.69	-9.09
4	Mulch	34.78	25.31	-9.47	30.19	-4.59	15.59	-19.19

TABLE 6  
*Nitrification of solutions when inoculated from mulched and unmulched soils (32-day test)*

GREENHOUSE TREATMENT	INOCULATION FROM FLATS MULCHED IN FIELD		INOCULATION FROM FLATS UNMULCHED IN FIELD	
	Nitrogen as nitrate	Nitrogen oxidized	Nitrogen as nitrate	Nitrogen oxidized
	mgm.	per cent	mgm.	per cent
No mulch.....	2.59	25.9	2.89	28.9
Mulch.....	2.04	20.4	1.98	19.8

#### STUDIES WITH NITRIFYING SOLUTIONS

These same soils were sampled after 10 weeks and inoculations made from them into sterile solutions in the laboratory, in order to test the change of 10 mgm. of nitrogen as ammonia to nitrates in 32 days. In each case, the change to nitrates was greater in flasks inoculated with the unmulched soil, as shown in table 6. The ammonia nitrogen was more slowly oxidized when inoculations were made from soil under the mulch. This suggests that the presence of the mulch influences the nitrifying flora so that their activity is lessened possibly through decreased numbers or lessened virulence.

## SUMMARY

A careful study in the field and in the greenhouse of the causes of low nitrate accumulation in a soil under straw mulch as compared with the nitrate accumulation in the same soil without mulch has shown that:

1. The failure of nitrates to accumulate is not due to a shortage of ammonia nitrogen, since this is present in larger quantities under the mulch than in soil not mulched.
2. Aerating the mulched soil increased nitrate accumulation.
3. Modifying the structure of the mulched soil by air-drying and remoistening gave a marked increase in nitrate accumulation.
4. Air-drying and remoistening coupled with aeration, gave the highest nitrate accumulation.
5. Applying the mulch increased the soil moisture content and brought on a marked change in soil structure, with less granulation and poorer tilth.
6. Soil, used as inoculum, from the plot under the mulch had a much lower nitrifying efficiency as measured by change of ammonia to nitrate in solution.
7. Reducing the moisture content of the soil under the mulch to that of the soil without mulch gave a slight increase in nitrates, while raising the moisture of the unmulched soil to that of the mulched gave a decided decrease in nitrates. This decrease, however, was prevented by aeration. This emphasizes that the mulch exerts some force on depressing nitrate accumulation through lessened aeration as a result of increased soil moisture.
8. Removing the mulch gave a marked increase in nitrate accumulation after 2 months, while its application to a previously unmulched soil brought on a marked decrease in the same time even though the moisture remained unchanged.

## CONCLUSIONS

These facts all indicate that the straw mulch, in applications as heavy as 6 tons per acre, cuts down evaporation, thereby increasing the moisture, lowering the temperature and preventing the normal exchange of air, all of which induce a poor physical condition and unfavorable environment for nitrate accumulation.

Accompanying these physical changes there may be some significant chemical factors, as change in solubilities as a result of drying as shown by Gustafson (9), or other factors, since Lebedjantzev (13) believes that the yielding power of a soil is maintained by alternate wetting and drying; but nevertheless, the mulch brings on the changed physical conditions which depress the nitrate accumulation, and the removal of which restores the normal nitrate activities.

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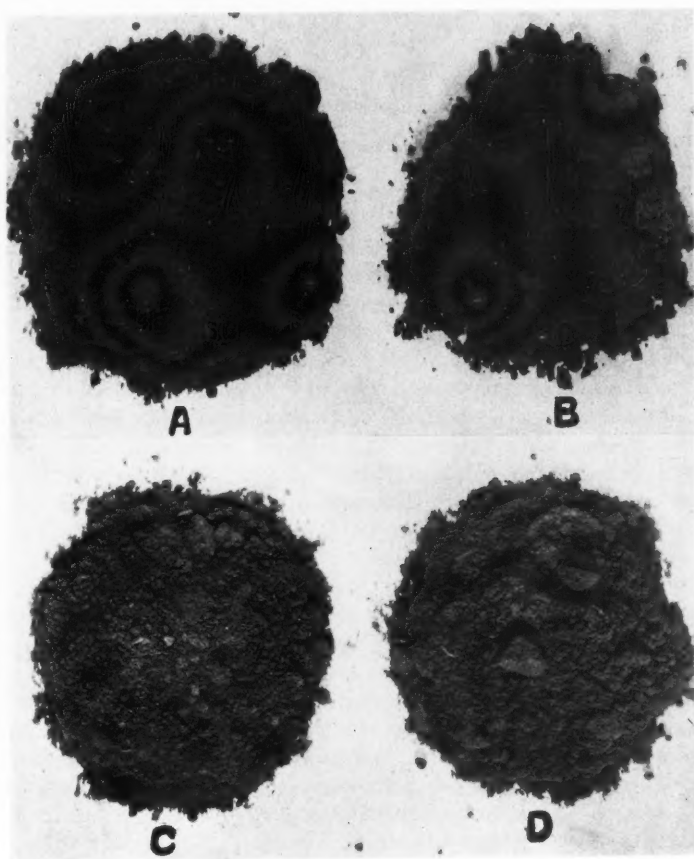


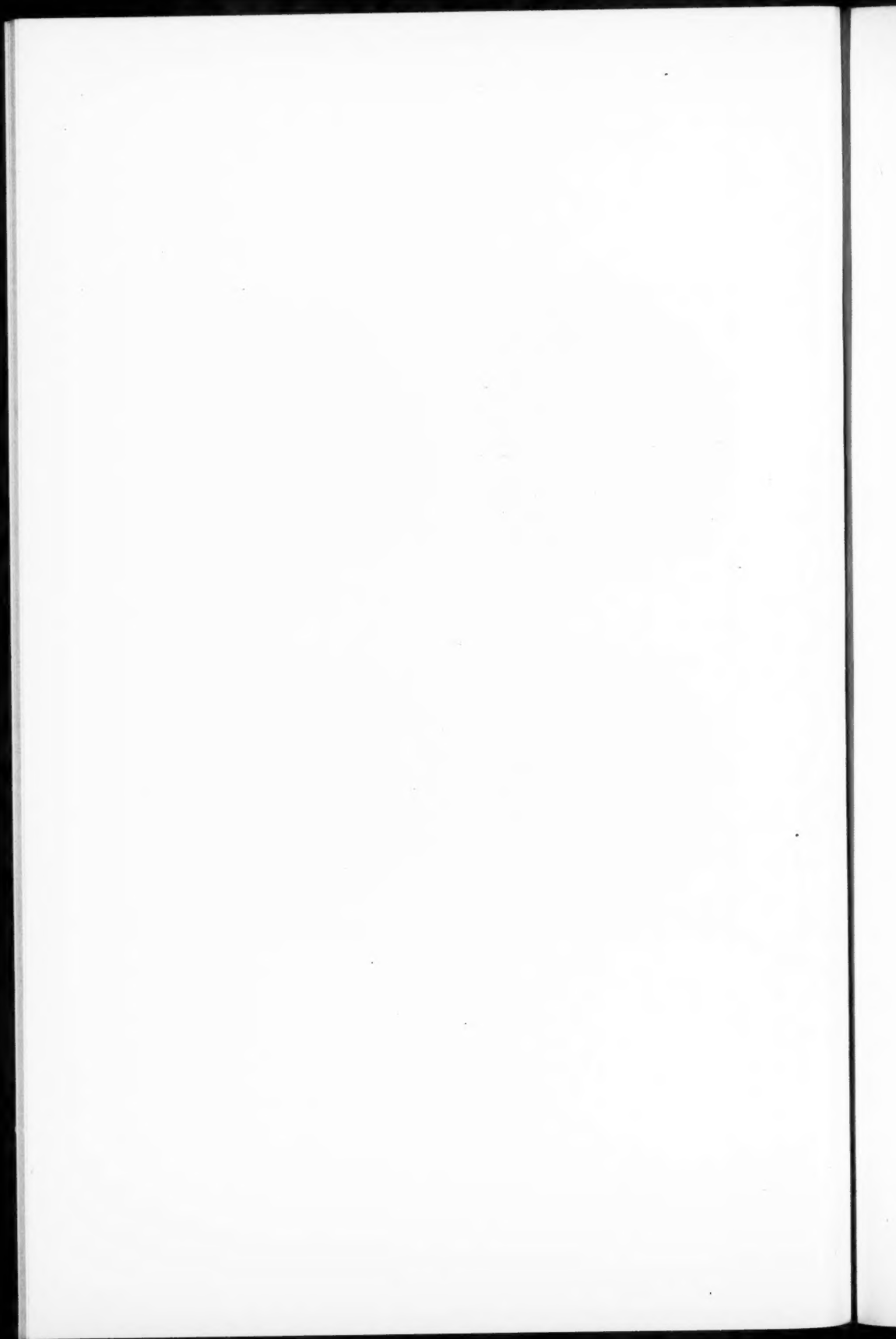
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PLATE 1

DIFFERENCES IN STRUCTURE OF SOIL AS A RESULT OF MULCH

- A. Soil from unmulched plot (15.04 per cent water).
- B. Soil from mulched plot (22.0 per cent water).
- C. Soil from unmulched plot 3 months after being air-dried and remoistened (15.07 per cent water).
- D. Soil from mulched plot 3 months after being air-dried and remoistened (21.53 per cent water).







## RELATION OF BIOLOGICAL PROCESSES TO CATION CONCENTRATIONS IN SOILS

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For several years past, the writer has used a process of water displacement to obtain soil solutions. Such solutions are readily obtained from sandy loam soils when these are displaced at moisture contents approximating their optimal requirements for plant growth, even if substantial amounts of colloidal material are present. When the successive increments of solutions thus obtained have equal concentrations, as is usually the case, the solution as a whole has many of the properties which the true soil solution should possess, as inferred from observations of freezing point depressions made directly on the soil, from water extractions, etc. The evidence upon which this conclusion is based is discussed elsewhere (1, 2), and need not be further considered here. Suffice to say that this evidence is, in the author's opinion, ample to justify the belief that such solutions are either very closely representative of, or actually identical with the true soil solution; always provided that the successive increments of displaced solution do not vary materially in concentration.

In the course of studies of displaced solutions, it early occurred to the writer that soils depleted of dissolved matters by the displacement process might be re-examined later, or after appropriate treatments, to determine the effect of time or treatments upon the concentration in the liquid phase. It was also obvious that the same procedure might be applied to advantage to differentiate between the effects upon all constituents of the liquid phase of soils, of solution processes as such, and of biological activities, and to bring out the differences between the results of biological oxidation and reduction.

The carrying out of such experiments seemed desirable, because of the apparent, perhaps natural, tendency of studies in this field to regard determinations of the concentration or rate of formation of some specific end product of soil activities, such as nitrate, as conclusive of the effect upon soil fertility of the processes involved; whereas the author has long believed that these latter have a more general significance. In any event, the methods hitherto available have not been adequate to measure the effects of soil activities upon the concentrations of certain types of constituents, notably the cations commonly originating in the solid phase. Information as to the effects of soil activities is thus pretty definitely limited to their influence on anion composition. In

the case of experiments involving biological oxidations, there are only scattered observations that total concentration and calcium ion usually increase with nitrate or sulfate formation. Still less information is available as to the effect of biological reductions upon total or cation concentrations. Furthermore, such information as is available concerning the secondary results of biological processes is largely based upon water extractions which must be regarded as inadequate if definite quantitative relations are to be developed.

The object of this paper is to report and discuss the results of several sets of experiments suggested by the above considerations. One set of experiments has to do with quantitative comparisons of the effects upon the liquid phase of soils of solution processes *per se*, as distinguished from those accruing from biological activities; the other is concerned with the relation of cation to anion concentration as affected by biological processes.

For the first of these purposes, it is necessary to consider in some detail the observed behavior of soils with reference to the concentration of the liquid phase separated during the process of water displacement. As stated heretofore, the successive portions of solution displaced from soils tend to have equal concentrations. This condition, of course, does not continue indefinitely, and at some point, depending upon such properties as the character of the soil, dimensions of the soil column, and amount of water initially present, the concentration begins to fall, because of the admixture of displacing water with the residual liquid phase. By experience, the author has found that with 2 kgm. of sandy loam soil at optimum moisture, tightly compacted in tubes approximately three inches in diameter, dilution of the displaced solution seldom occurs until two-thirds or more of the initial volume of water in the soil column has been recovered. Figure 1 based on determinations of the specific resistances of successive 10-cc. portions, represents the characteristic behavior in a soil which lends itself to the displacement procedure.

Inspection of this figure clearly differentiates a zone of constant concentration where the specific resistances remain at approximately 200 ohms.<sup>1</sup> This zone has been designated the "Soil Solution" and is regarded as representing the liquid phase of the soil as it exists in place. After twenty-six 10-cc. portions out of the 310 cc. of water initially present in the packed soil have been collected, there is a sharp increase of resistance indicating greatly diminished concentrations. From this point on, there is a relatively rapid increase of resistance to about 4,000 ohms, when sixty-two 10-cc. portions, equivalent to 200 per cent of the initial moisture content of the soil, have been collected. It is evident that the solutions obtained after the observed break noted above represent mixed effects. The first portions are obviously made up largely of the pre-existing liquid phase with small proportions of displacing water. The later portions, conversely, must consist of small portions of the pre-existing liquid phase and large proportions of displacing water. In addition, there

<sup>1</sup> The absolute values noted apply, of course, only to the particular soil under observation, but the form of the figure is characteristic of the general behavior.

is doubtless a certain amount of material being dissolved from the solid phase particles by the progressively diluted liquid phase. The amounts of such newly dissolved material must be extremely small as indicated by the high resistances observed in the last portions collected. For convenience, it seems rational to differentiate further a "Zone of Admixture" where the concentration is determined primarily by the residual liquid phase not removed as soil solution. Such a zone should include the portions collected after the resistances begin to increase and until an amount of displacing water, sufficient to have removed most of the pre-existing liquid phase, has passed through the core of soil. This zone in the present case would presumably include the twenty-seventh to thirty-sixth portions (twice the difference between the

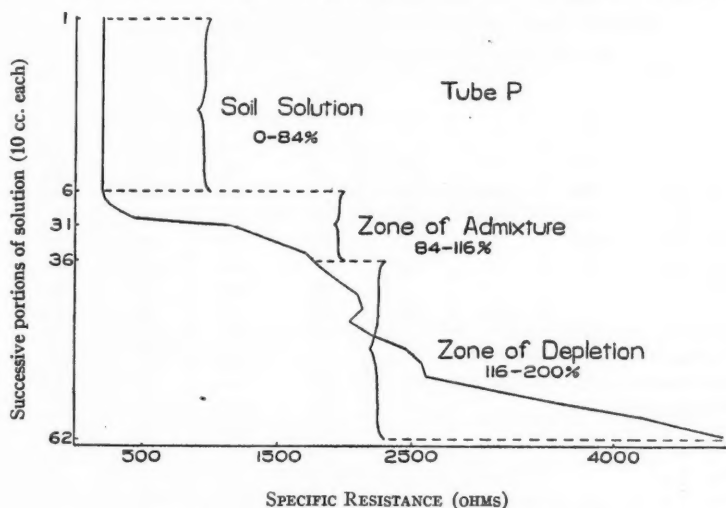


FIG. 1. DISPLACED SOLUTIONS FROM SANDY LOAM SOIL

volume collected when the break in concentration occurs, and the volume equivalent to 100 per cent recovery.) The specific resistance of the twenty-sixth portion is 199 ohms, equivalent to an approximate concentration of 3885 p.p.m., that of the thirty-sixth portion is 1760 ohms equivalent to a concentration of 365 p.p.m. The portions collected subsequent to the thirty-sixth obviously include only a small portion of the previously existing liquid phase plus the small amounts of material dissolved *pari passu* by the displacing water. These we designate the "Zone of Depletion."

From these results, it is obvious that if displacement is discontinued at any convenient point after the soil solution has been obtained, the liquid phase will have reached a comparatively low concentration throughout the soil mass, but will vary relatively in that the solutes, originally present and uniformly distributed, will have moved downward in the soil column. The concentration of

the liquid in the upper part of the column is then determined almost exclusively by the very small amounts of new material dissolved from the solid phase by displacing water after the removal of the original liquid phase. The concentration of the liquid in the lower part of the column, on the other hand, will be determined by the amount of material derived from the original liquid phase which still remains in the system. It is evident that the concentrations observed in the Zone of Admixture and the Zone of Depletion represent the actual concentrations as they exist in the soil from the lower part of the column upward under the conditions stated, i.e., just after the removal of the soil solution. It is further evident that the actual concentrations at the various levels

TABLE 1  
Specific resistances (ohms) of successive portions of displaced solutions  
Soil 8 (2 Kilos at 15.5 per cent  $H_2O$  = 310 cc. of liquid)

	TUBES						
	B	C	D	E	F	G	H
1st 10 cc.	196	197	203	197	195	190	193
2nd 10 cc.	197	195	196	192	187	188	187
11th 10 cc.	189	191	189	191	193	188	...
16th 10 cc.	193	193	193	193	193	190	189
21st 10 cc.	193	190	190	191	193	187	188
22nd 10 cc.	...	...	...	190	188	188	188
23rd 10 cc.	...	192	196	195	190	192	192
24th 10 cc.	212	...	...	190	191	189	193
25th 10 cc.	...	...	...	...	194	193	197
26th 10 cc.	...	204	202	199	202	203	207
27th 10 cc.	...	...	...	214	220	226	226
28th 10 cc.	...	...	...	255	246	277	269
29th 10 cc.	...	...	...	349	324	383	348
30th 10 cc.	...	...	...	538	471	556	563
31st 10 cc.	...	...	...	918	828	909	686

of any soil column in which displacement is discontinued, may be inferred from the results obtained from a similar column in which the displacement is continued beyond the point at which the first displacement was stopped. When the conditions existing in soil columns in which the displacement is initially limited to removal of a volume of solution equal to the amount of water in the soil core are known, the effect of subsequent treatments of such soil may be measured by additional displacements after the treatments have been imposed.

#### PLAN OF EXPERIMENT

A number of 2-kgm. portions of a well-mixed sandy loam soil moistened to 15.5 per cent water were displaced in the manner usual in this laboratory (1). The displacements of all of these, save two, were discontinued and the excess water on top of the soil columns was discarded when 310 cc. of solution equiv-

TABLE 2

*Treatment of soil portions after first displacement and preceding other displacements*

TUBE	SECOND DISPLACEMENT*	THIRD DISPLACEMENT*	FOURTH DISPLACEMENT*
P	No intervening treatment. Second displacement (100 to 200 per cent) immediately after first displacement		
X	No intervening treatment	Displacement continuous up to 300 per cent of initial moisture	
E	Packed soil kept at 0°C. for 11 days		
B	Packed soil 2 months at laboratory temperature		
C	Packed soil, 2 months at laboratory temperature	Packed soil, 3 months at laboratory temperature	Soil removed from tube, aerated, kept at constant moisture at laboratory temperature for 14 months
D	Packed soil, 2 months at laboratory temperature	Packed soil, 2 months at laboratory temperature plus 1 month at 39°C.	Soil removed from tube, aerated, kept at constant moisture at laboratory temperature for 14 months
F	Packed soil, 2 months at laboratory temperature plus 1 month at 0°C.	Soil removed from tube, aerated, kept at constant moisture at laboratory temperature for 14 months	
G	Packed soil, 2 months at laboratory temperature plus 1 month at 39°C.	Soil removed from tube aerated, kept at constant moisture at laboratory temperature for 14 months	
H	Packed soil, 3 months at laboratory temperature	Soil removed from tube, aerated, kept at constant moisture at laboratory temperature for 14 months	

\* Each displacement represented an amount of solution equal to the moisture present before displacing water was added, i.e., 15.5 per cent of 2 kgm.

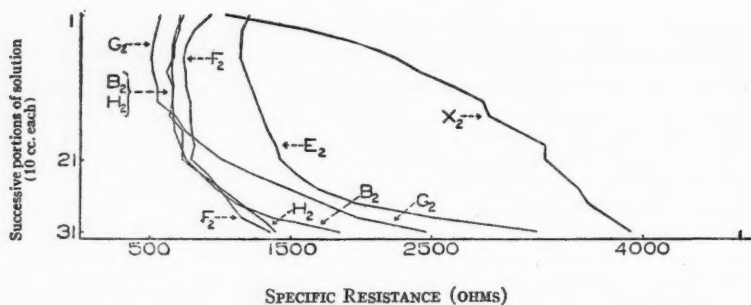


FIG. 2. SECOND DISPLACEMENT, 100-200 PER CENT OF INITIAL MOISTURE CONTENT

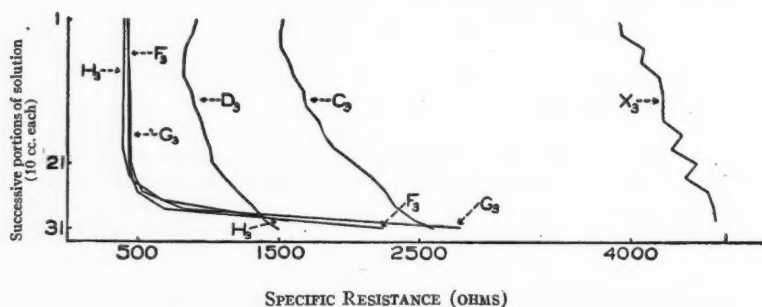


FIG. 3. THIRD DISPLACEMENT, 200-300 PER CENT OF INITIAL MOISTURE CONTENT

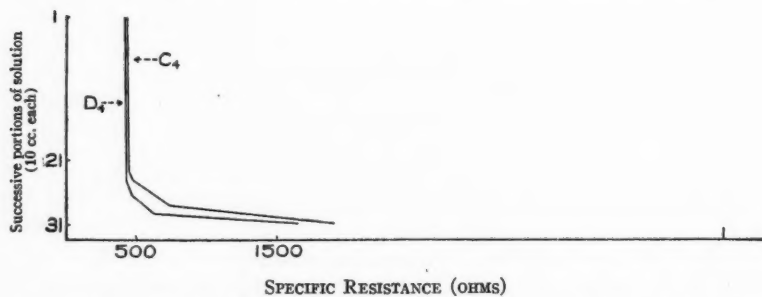


FIG. 4. FOURTH DISPLACEMENT, 300-400 PER CENT OF INITIAL MOISTURE CONTENT

alent to 100 per cent of the initial moisture content of the soil, was obtained. The displacement of the two remaining tubes was continued until the solution amounted to 200 per cent and 300 per cent, respectively, of the initial moisture contents of the soil (tubes P and X). The results of the displacement up to 200 per cent have been discussed above. The results of the 100 per cent displacements are shown in table 1.



Study of table 1 shows that the concentrations are, with a few sporadic exceptions, very uniform in the successive portions from all displacements up to the twenty-sixth, representing a recovery of 84 per cent of the soil solution. The rapid decrease in concentration between the twenty-sixth and thirty-first portions further shows that the residual 16 per cent of the soil solution is being diluted and removed from the system.

At this stage, the soil in the tubes is, of course, saturated with moisture derived from the displacing water used in the procedure, plus the small amount of residual soil solution. The subsequent procedure consisted in maintaining the various tubes at constant moisture and under conditions regarded as inhibitive or stimulative of solution processes, making further displacements from time to time. The treatment of the various tubes of soil is indicated in table 2.

The data representing the specific resistances of the successive portions of solution are shown in figures 2, 3, and 4, respectively, for the second, third and fourth displacements.

#### DISCUSSION OF RESULTS OF SECOND DISPLACEMENT

The data from the soil in tube  $X_2$  represent the norm for comparison, since, in this case, the second displacement immediately followed the first. In all other tubes, the displacement was delayed for varied intervals of time. From the figure, it is apparent that two effects have resulted from the delays: One is a tendency toward equalization of concentration in the successive portions of solution; the other is a change of the total concentration of electrolytes.

As stated heretofore, the soil in all tubes was saturated with water, precluding strictly aerobic processes. In addition, it should be kept in mind that practically all the nitrates of the pre-existing soil solution had been removed from all tubes during the first displacement. Thus the material most susceptible of being acted upon by reducing agencies had been almost entirely eliminated. It seems reasonable to infer, therefore, that anaerobic processes had also been largely and perhaps entirely suppressed in all tubes. Furthermore, as regards  $E_2$  and, for a part of the time interval  $F_2$ , it would seem that biological activities must have been absolutely precluded because of the low temperatures at which the soil in these tubes was maintained.

Figure 2 shows that tube  $F_2$ , which had the same treatment as tube  $B_2$ , (2 months at laboratory temperature), except that it was maintained for a third month in the frozen condition, had lower concentrations of electrolytes than those of tube  $B_2$ . The decreases observed, if significant, would appear to be due to some change in the solid phase incidental to freezing and thawing. The elucidation of the cause of such an effect is beyond the scope of the present investigation, and for our purposes, it will suffice to point out that in the cases where freezing was utilized to obviate more completely the possibility of biological activities, the observed concentrations probably represent minima. Thus the results from tube  $E_2$  (11 days at  $0^\circ\text{C}.$ ) possibly represent somewhat lower concentrations of electrolytes, due to this freezing effect, than would

have been obtained, assuming absence of biological activities, if the freezing had been omitted. In comparing  $E_2$  and  $X_2$ , it seems fair to conclude that there has been a substantial gain of concentration, even in the short period of 11 days, which is due to dissolution of solid phase material and which was very definitely *not* brought about by biological activities.

In the case of  $B_2$ ,  $C_2$ ,  $D_2$ ,<sup>2</sup> 2 months at laboratory temperature saturated with water, there was a still greater gain of concentration. Here the effect of freezing and thawing was eliminated but the observed gain may be ascribed with considerable confidence to solution processes alone. An additional month at laboratory temperature did not, however, induce further solution of solid phase material, the results from tube  $H_2$  being substantially the same as those from tubes  $B_2$ ,  $C_2$ , and  $D_2$ . When the temperature was raised for the third month of the period ( $G_2$ ), there was a definite increase in concentration of the earlier portions of solution, but the later portions had lower concentrations and it is not clear that the increase in temperature had any effect other than to cause an accumulation of solutes in the lower part of the tube.

We conclude from the conditions to which the various tubes were subjected prior to the second displacement and from the results of that displacement, that a substantial increase in the concentration of the liquid phase of depleted soils may be caused by the inherent solubility of solid phase materials. It is obvious, however, that even under the most favorable conditions the increase is only relative and that the total concentration of depleted soils remains very low in the absence of biological activities.

#### DISCUSSION OF RESULTS OF THIRD AND FOURTH DISPLACEMENTS

The concentration of the earlier portions of the second displacement have doubtless been affected to some extent by the small proportion of the original soil solution not removed by the first displacement. During the second displacement, however, the residuum of soil solution remaining from the first displacement must have been removed together with an additional quota of material dissolved from the solid phase. The results from the third displacement, therefore, represent the condition in soils which had reached an extreme degree of depletion.

When we compare  $C_3$  and  $D_3$  with  $X_3$ , it is evident that in soils which are practically exhausted of dissolved materials a relatively large increase of concentration in the liquid phase may occur, even in the absence of biological activities in the period of 1 month at laboratory temperature. At the low concentrations in question here, the effects of increased temperature appear to be relatively important (*Cf.*  $C_3$  and  $D_3$ ).

In the second displacement, we have shown that after 2 months at laboratory temperature, there is no substantial increase of concentration in the absence of

<sup>2</sup> Results from tubes  $C_1$  and  $D_1$  were practically identical with those of tube  $B_1$ . It was impossible to plot them in the figure because of the merging of the lines on the scale used.

biological activities (Cf. H<sub>2</sub> and B<sub>2</sub>). This raises the presumption that the system had reached equilibrium for the conditions to which the soil had been subjected. A similar comparison for the third displacement is not available, but it is highly probable that C<sub>3</sub> represents substantial equilibrium in the absence of increased temperatures or biological activities. It would appear that the difference between the concentrations indicated in X<sub>3</sub> and C<sub>3</sub> probably represents the order of magnitude of the concentration changes which are likely to occur in greatly depleted soils at ordinary temperatures unless biological activities are brought into play. The average resistance (first 26 portions, corresponding to the zone of the soil solution) of X<sub>3</sub> is 4202 ohms and of C<sub>3</sub> is 1785 ohms. The relative change of resistance is large but the absolute concentrations corresponding to these resistances are 135 p.p.m. and 355 p.p.m., and while this is also relatively great, it is evident that the absolute change is insignificant as compared with the concentration of the undepleted soil which amounted to 3885 p.p.m. with a specific resistance of 199 ohms (See first displacement, figure 1).

We have now to consider the changes produced when the conditions in the various portions of soil were made favorable to biological activities. As indicated in table 2, the soil from tubes F, G, and H after the second displacement, and that from tubes C and D after the third displacement, was removed and each portion made homogeneous by mixing. The various portions were maintained at constant moisture but stored loosely in Mason jars, permitting the access of air for an additional period of 14 months.

The effects of the treatment of the two sets of soil are remarkably uniform. In the first place, the mixing of the various portions has rendered them homogeneous, so that the successive portions of solution obtained have equal resistances up to a point corresponding very well with the break shown for the original soil in figure 1. Secondly, the concentration of electrolytes as shown by the resistances of the solution obtained from tubes F<sub>3</sub>, G<sub>3</sub>, and H<sub>3</sub> (to approximately 1800 p.p.m.) is enormously increased in absolute value over that shown by tube C<sub>3</sub> (355 p.p.m.) where biological activities were presumably precluded. Thirdly, similar determinations upon the solutions from C<sub>4</sub> and D<sub>4</sub> (fig. 4) show that these are practically identical with those obtained from F<sub>3</sub>, G<sub>3</sub> and H<sub>3</sub>. It is evident that the greater depletion of the former set has not prevented as complete a recovery of concentration as that shown in the latter. It would appear that the power of recovery of soils after the removal of the original liquid phase and when placed under conditions favorable to biological activity, is unaffected by further leaching, subject, of course, to the limitation that if leaching is continued to the point where a solid phase constituent is entirely removed from the system, the equilibrium concentration may be directly and indirectly affected. Obviously, it is the character of the residual solid phase, organic and inorganic, which determines the concentration to which the liquid phase of a given soil will eventually return under conditions in other respects favorable to biological activity.

## OXIDATION AND REDUCTION EXPERIMENTS

The preparation of the soil for the oxidation experiment consisted in very thoroughly leaching a portion of soil, which had a high concentration in its liquid phase, and mixing this with another portion of the same soil which had not been leached. The proportion of leached to unleached soil was 4:1. The reason for this method of preparation, rather than that of merely leaching the entire amount of soil was, of course, to ensure the retention of an active flora and a certain amount of dissolved organic matter. The mixed, partially depleted soil was brought to optimum moisture and allowed to come to equilibrium in relation to its water content (3 days). Portions of this stock soil were then displaced and the remainder maintained at constant moisture under aerobic conditions for a period believed to be adequate for a substantial increase of nitrate content, when this also was displaced.

TABLE 3  
*Displaced solutions from sandy loam soil before and after biological oxidation*

MOISTURE  <i>per cent</i>	REACTION  <i>pH</i>	SPECIFIC RESISTANCE  <i>ohms</i>	CONCENTRATION OF ELECTROLYTES*							
			NO <sub>3</sub>	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	Na	K
			4.94†	1.28	3.55	4.34	9.48	3.37	3.00	1.23
16.5	7.3	747	307.00‡	78.00	126.00	209.00	190.00	41.00	69.00	49.00
16.1	7.2	497	668.00‡	50.00	120.00	271.00	242.00	63.00	104.00	58.00
			10.76†	0.82	3.38	5.64	12.08	5.18	4.52	1.48

\* Determinations of phosphate and silicate were omitted as unessential for present purposes. More comprehensive studies should, of course, include these constituents.

† Milliequivalents.

‡ Parts per million.

The reduction experiment was performed on the same soil as was used in the preparation of the stock soil for the oxidation experiment. The soil was brought to optimum moisture and packed in the displacement tubes preparatory to making the displacement in the usual manner. Certain of these packed soils were displaced at once. The remainder were retained for a period of time believed to be sufficient to ensure considerable reduction of nitrates. (The conditions in the tubes were, of course, anaerobic, because the air was forced out during the packing of the fairly moist soil.) At the proper time, these also were displaced.

The soil used in both of these experiments was a sandy loam, known as "no. 10" in this laboratory. The data are presented in tables 3, 4 and 5.

These data show that the moisture contents of the soil before and after biological oxidation did not vary greatly, thus obviating the necessity for correcting the figures obtained in the last displacement to compensate for the changed moisture content. It should also be noted that the pH values are within the experimental error of this determination and may, therefore, be regarded as

identical. The fluctuations of other constituents are, therefore, not assignable to measureable changes in the degree of acidity of the system.

The most obvious and characteristic effect of the biological oxidation process is a marked increase of nitrates, and a substantial increase of sulfates. The only compensation<sup>3</sup> for these increases is a small decrease of bicarbonate concentration. Under these circumstances, it is evident that total and cation concentration must have increased, and this is borne out by the figures which show substantial increases of calcium, magnesium, sodium, and potassium. We do not suggest that all cations will necessarily increase in all soils when similarly treated, since secondary reactions and hydrolyses may affect the behavior of individual cations.

In the light of the effects shown on our soil, the question naturally arises as to whether biological oxidations resulting in substantial increases of nitrate concentration are, in general, accompanied by increases of total and cation concentration. This must necessarily be answered in the affirmative unless concurrent losses of sulfate or bicarbonate, or both, occur in amounts sufficient to offset the gain in nitrate concentration. It is conceivable that the oxidation of ammonia to nitrate may, under certain circumstances, take place at the expense of the oxygen of the sulfate, and it is known that the nitrifying organisms use carbonates in solution cultures. On the other hand, the aerobic conditions under which the nitrification process thrives are also favorable to the oxidation of sulfur, and in the absence of definite evidence of sulfate losses, it seems reasonable to infer that these would not occur under conditions favorable to nitrate formation. It is not quite so clear that losses of bicarbonate sufficient in amount to offset the gain of nitrate may not occur in soils where the equilibrium conditions, including the reaction, permit of high concentrations of this ion. Such conditions seldom exist, however, except in soils which are very alkaline, and it seems reasonable to infer that compensatory losses of bicarbonate are not ordinarily sufficient to offset the increase of nitrates in acid, neutral, and even somewhat alkaline soils. We conclude, therefore, that biological oxidations generally tend to increase the total concentration of the soil solution and in effect determine the cation as well as the anion concentration.

The exact mechanism of the solution of positive components is, of course, not explained by our results. It is probable, in spite of the fact that there is no increase of acidity in the displaced solution as a whole, that there is a temporary increase of H-ion concentration at interphase boundaries which releases such elements as calcium and magnesium, from the mineral components and that these cations continue in solution because of the presence of the nitrate and sulfate, and of bicarbonate to the extent to which the equilibrium conditions permit.

Temporary, or highly localized increases of acidity could be accounted for by an increase of CO<sub>2</sub> in the soil atmosphere, a condition which has been

<sup>3</sup> The slight decrease of chloride is obviously within the limits of experimental error.



repeatedly observed during biological oxidations (5, 6) and indeed is a necessary result of the utilization of organic carbon by the soil organisms. The low concentrations, and the actual decrease of bicarbonate are presumably without general significance in this relation, inasmuch as the concentrations here observed probably represent merely the equilibrium between  $\text{CO}_2$  and  $\text{HCO}_3^-$  for the particular system.

The results from the reduction experiment are in interesting contrast to those just discussed.

Here it will be observed there is a very great decrease of nitrate without an equivalent decrease of cation concentration, the loss of nitrate being compensated for by very large increases of bicarbonate and what appear to be significant gains of sulfate concentration. There is an extraordinary similarity in these changes to those occurring in soils under crop, where it has been shown that at the end of the growing season, nitrates have practically disappeared,

TABLE 4  
*Displaced solutions from sandy loam soil before and after biological reduction*

MOISTURE  <i>per cent</i>	REACTION  <i>pH</i>	SPECIFIC RESISTANCE  <i>ohms</i>	CONCENTRATION OF ELECTROLYTES*							
			$\text{NO}_3^-$	$\text{HCO}_3^-$	Cl	$\text{SO}_4^-$	Ca	Mg	Na	K
18.4	7.1	374	13.49†	1.19	9.25	2.77	16.51	7.97	5.05	1.99
18.4	7.6	409	838.00‡	73.00	328.00	133.00	331.00	97.00	116.00	78.00
			42.00‡	664.00	324.00	156.00	242.00	67.00	127.00	67.00
			0.68†	10.89	9.14	3.24	12.08	5.51	5.52	1.72

\* Determinations of phosphate and silicate were omitted as unessential for present purposes. More comprehensive studies should, of course, include these constituents.

† Milliequivalents.

‡ Parts per million.

cations have been substantially decreased, but bicarbonate and pH values increase (2). It is well demonstrated that when the higher plants are concerned, the bicarbonate eliminated through the plant roots is an important factor in such relations (4), and it now appears that the  $\text{CO}_2$  produced by soil organisms may bring about similar effects.

The increased bicarbonate concentrations shown in our data indicate that  $\text{CO}_2$  is produced even under anaerobic conditions and presumably by the very organisms concerned with nitrate reduction. If  $\text{CO}_2$  is an end product of such reductions, it seems probable that the soil solutions of soils in general are not likely to suffer very great depletion of cation concentration during denitrification. Such a condition tends to explain why the enormous variations of nitrate concentration (5, 6, 7) which have been observed in soils within short time intervals, may have very little effect upon plant growth, inasmuch as the concurrent fluctuations of other constituents and particularly the less slowly absorbable cations are probably small.



The increase of sulfate concentration is difficult to explain unless sulfate oxidation and nitrate reduction are reciprocal processes. Such a relation has been shown (3) for certain organisms under aerobic conditions and there is no inherent reason why it may not occur in the absence of air. Although no stoichiometric relation is here shown, the result suggests that sulfates commonly may increase when nitrates are lost and thus tend to offset the losses of the latter in their effect upon total and cation concentration.

In the reduction experiment considered above, it was shown that when the amount of reduction was substantial in that the nitrate concentration was greatly diminished, there was some decrease of total and cation concentration, but that this was by no means proportional to the loss of nitrate. We happen to have at hand other data, from an experiment in which the conditions were neither completely nor continuously favorable to one process to the exclu-

TABLE 5  
*Displaced solutions from sandy loam soil before and after excessive wetting*

MOISTURE	REACTION	SPECIFIC RESISTANCE	CONCENTRATION OF ELECTROLYTES									
			NO <sub>3</sub>	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	PO <sub>4</sub>	SiO <sub>3</sub>	Ca	Mg	Na	K
per cent	pH	ohms	6.63†	0.79	12.80	3.68	0.01	1.13	11.78	3.78	9.22	0.67
15.1	7.3	389	412.00‡	48.00	454.00	177.00	1.17	43.00	236.00	46.00	212.00	26.00
15.5*	7.2	368	339.00‡	85.00	452.00	334.00	1.33	32.00	288.00	51.00	223.00	30.00
			5.46†	1.39	12.75	6.95	0.01	0.84	14.37	4.19	9.70	0.77

\* Moistened to approximately 18 per cent, but found to be too wet. Spread out to dry for 4 days. Packed and displaced on fifth day.

† Milliequivalents.

‡ Parts per million.

sion of the other, which show that there may be an actual increase in total and cation concentration if the amount of nitrate is not greatly diminished. These results are shown in table 5. Otherwise than just stated, the indications are the same as those observed in the preceding experiment. It will be noted that nitrates diminish concurrently with increase of bicarbonates and substantial increases of sulfates. The large absolute and relative charges of sulfate concentration observed under the special conditions of this experiment merit attention and suggest the importance of this ion in maintaining cation concentrations at a relatively high level in soils where nitrates are diminishing.

#### GENERAL DISCUSSION

When we consider the multiplicity of observations which tend to show the indispensable character of biological factors in favorably affecting soil fertility, it may, perhaps, appear superfluous to demonstrate a correlation between biological activity and the total concentration of the liquid phase of soils. The

data presented in the early part of this paper, however, show how very low the total concentration of the liquid phase of a typical mineralized soil remains unless the anions characteristic of biological oxidations are brought into play. Such evidence makes it quite clear that the nitrate, sulfate, and bicarbonate formed during such oxidations must determine largely the cation concentration of the soil solution and may thus have important effects on plant growth, quite apart from the physiological properties of the nitrogen or sulfur thus made accessible to the plant.

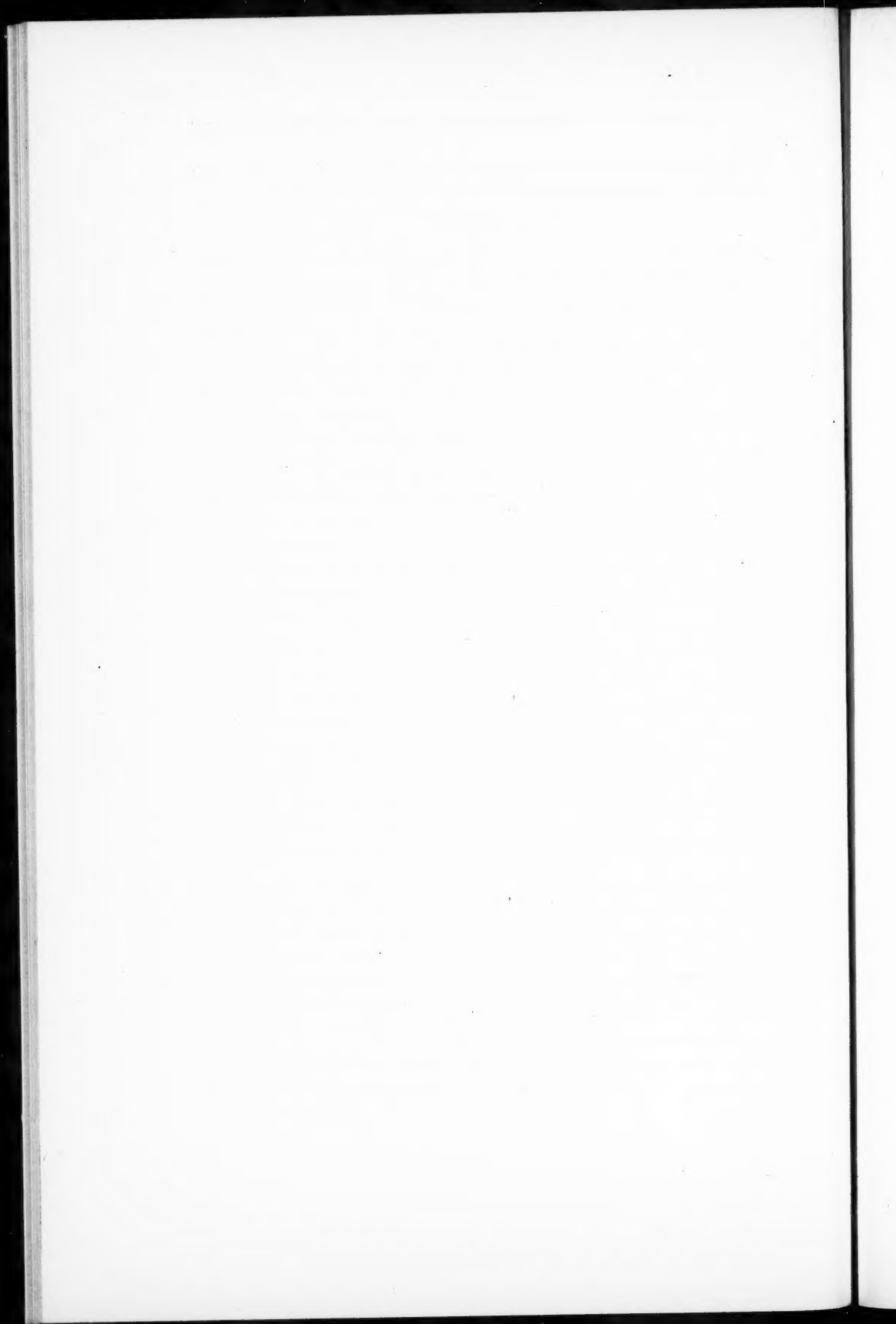
Of the anions concerned, the data shown in tables 3 and 4 indicate that when nitrate concentrations are high, i.e., after intensive biological oxidation or before reduction, the amount of this constituent is the most important element in determining cation concentration. Conversely, when nitrates are low, i.e., after reduction, or in the case of depleted soils, before oxidation, sulfates and bicarbonates exercise in this respect a predominating influence. As stated heretofore, we have shown this same effect elsewhere as between the conditions existing in soils under crop at the beginning and at the end of the growing season, and it is evident that nitrate concentrations alone neither determine nor indicate the cation concentrations at the critical periods of plant growth. Obviously, from all of the data, we may conclude with considerable confidence that if the nitrate concentration is high, as in the early part of the season, the usual decrease of this ion incidental to cropping is to a considerable degree compensated in its effect upon cation concentration by the other anions originating in biological processes or excreted by plant roots. On the other hand, the nitrate equilibrium concentrations of many soils are low, and although such a soil may, because of a high rate of formation of nitrate and the rapid absorption of nitrate ion by plants, be enabled to meet the requirements of plants for nitrogen; it may not be able to maintain high enough concentrations of other solutes to ensure that these will enter the roots at a sufficiently rapid rate to satisfy the requirements of the plant. In such a soil, the rate of formation of sulfates and carbon dioxide, or the equilibrium concentrations with respect to sulfate and bicarbonate may, by determining cation concentration, control the growth of crops and thereby become the real limiting factor involved.

The above considerations also suggest that the large variation in nitrate content frequently observed in samples drawn within short distances of one another in the field may be without significance in terms of crop production. In the light of our results, changes in nitrate concentration are in general larger, both relatively and absolutely, than the concurrent changes in concentration of given cations in soils essentially homogeneous in the solid phase. Conclusions derived from observations of nitrate concentrations would not, therefore, appear to afford a secure basis for opinions as to the degree of variability of soils with respect to other constituents nor for determining the number of soil samples necessary to establish the significance of other data.

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# THE H-ION CONCENTRATION OF SOILS AS AFFECTED BY CARBONIC ACID AND THE SOIL-WATER RATIO, AND THE NATURE OF SOIL ACIDITY AS REVEALED BY THESE STUDIES<sup>1</sup>

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## INTRODUCTION

The effects of carbonic acid and the soil-water ratio on the H-ion concentration of soils have not been definitely established. Because of the important relationships that have been shown to exist between the H-ion concentration and many important chemical and biological processes in soils, the H-ion determination has become of great value in soil investigations. It is important, therefore, that any factors affecting the H-ion concentration of soils should be thoroughly studied. The purpose of this investigation was to study the effects of these two factors, namely, carbonic acid and the soil-water ratio; and, also, to discuss the nature of soil acidity in the light of the results obtained.

## METHODS USED IN THE H-ION DETERMINATION OF SOILS

### *General discussion of the electrometric and colorimetric methods*

Two general methods have been employed to determine the H-ion concentration of soils, namely, the electrometric and the colorimetric methods. The electrometric method was first applied to soils in 1914 by Fischer (7) in Germany, and later by Sharp and Hoagland (21) and by Gillespie (9) in this country. It is generally recognized as the most accurate of the two methods, but it has the decided disadvantage of being more tedious, of requiring more expensive apparatus, and of being unsuitable for soil extracts or other slightly buffered solutions. The colorimetric method, which has been developed largely in biological studies, is simple and requires inexpensive apparatus. It has been applied to soil extracts, however, with only a fair degree of accuracy.

In the electrometric determination of the H-ion concentration of soils, the soil suspension made from 1 part of soil to 2 parts of water is commonly used.

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The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Prof. E. Truog, under whose general direction this work was done.

The same ratio of soil to water is used in the colorimetric method, but with the latter the need of obtaining a clear solution for the color comparisons makes it necessary either to filter or to centrifuge the suspension.

Obtaining a clear extract has been apparently one of the main difficulties in the colorimetric determination. Most investigators have used the centrifuged rather than the filtered extracts, for filtering has quite generally been assumed to affect the H-ion concentration of the solution. Fisher (8) found that filtering through paper or Pasteur-Chamberland filters caused an increase of acidity as filtering proceeded. Truffaut (26) concluded from his work that colorimetric methods are usually inaccurate. He found that filtering by suction decreased the acidity of an acid soil. Bülman (3) determined the H-ion concentration of the filtered soil extracts colorimetrically and of the soil suspensions electrometrically, and reports differences on 7 soils as high as 0.6 pH.

Efforts to get good agreement between the H-ion concentration of centrifuged extracts, determined colorimetrically, and of soil suspensions, determined electrometrically, have not been very satisfactory either. Gillespie (11) found an average difference between the two methods of 0.08 pH, when applied to 57 soils. Individual differences ranged from + 0.3 to - 0.3 pH. Swanson (25) found that soil-water extracts had much lower H-ion concentrations than the soil suspensions. Carleton (4) in a similar comparison on 61 soils, using centrifuged extracts, found fairly good agreement, although one soil gave a difference of 0.55 pH, and 16 other soils gave differences ranging from 0.1 to 0.46 pH. Truffaut reports that in general with the colorimetric method, he obtained too high acidities, which he believes was due to the turbidity of the solutions obtained.

To remove the difficulty due to turbidity of soil extracts, various investigators have used flocculents. Gillespie (10) obtained fairly good results with the use of re-dialyzed colloidal iron as a flocculent, but does not recommend its use. He states that colloidal iron cannot be prepared entirely free from acids and, therefore, it might have a marked effect on slightly buffered soil extracts. Fisher (8) used calcium acetate, but, as would be expected from the addition of this salt, he obtained a decrease of the H-ion concentration.

Because of the conflicting conclusions of different investigations as to the accuracy of the colorimetric method in soil investigations, it was deemed desirable to make a study of this method in the preliminary work, and to compare it with the electrometric method.

#### *Details of the electrometric method used*

The electrometric method used was essentially that described by Clark and Lubs (6). The electrode vessel, however, was so constructed as to allow the hydrogen to enter not only from the side tube of the Cottrell H-electrode but also from the bottom of the vessel. This bubbling of hydrogen from the bottom kept the soil well in suspension and obviated the need of a shaking device. A Leeds and Northrup improved type of potentiometer and a sensitive



D'Arsonval galvanometer were used. Connection was made between the soil suspension and the saturated potassium chloride solution by means of an agar bridge. In the preliminary work it was found that the agar bridge may be a source of error. Thus, an agar bridge recently prepared was found to increase the H-ion concentration of the soil suspension. This was no doubt due to a slight diffusion of potassium chloride from the ends of the agar bridge. In subsequent determinations, therefore, care was always taken to soak the newly prepared agar bridge for one hour in conductivity water before using it and to keep it in contact with the soil suspension only while the successive readings were being made. The room was kept as nearly as possible at a temperature of 25° and corrections were made for deviations from this temperature. Both electrolytically prepared and commercial tank hydrogen were used with equal success, providing sufficient pressure could be obtained from each. It was found that if sufficient hydrogen could not be secured to bubble at a rate of about two bubbles per second, from both top and bottom of the electrode vessel, an erroneous reading was obtained. This may have been due to a difference in the pressure on the solution which, as shown by Loomis and Acree (14), may be a source of error, or to the failure to keep the soil particles well in suspension. When tank hydrogen was used, it was purified by passing through the train recommended by Truffaut (26).

*It should be emphasized, however, that the electrometric method cannot be used with soil extracts or displaced soil solutions, because these solutions are so slightly buffered that their H-ion concentration is easily affected by several factors which are difficult to control.* Thus it has been shown that a slight diffusion of potassium chloride from the agar bridge may even change the H-ion concentrations of soil suspensions, which are much more highly buffered than are soil extracts and soil solutions. Other factors, which may change the H-ion concentration of poorly buffered solutions are: impurities in the hydrogen, reduction of nitrates, and contaminated and so-called "poisoned electrodes."

#### *Details of colorimetric method used*

In the colorimetric method, the buffer mixtures and indicators used were those recommended by Clark (5). The indicators were ground with the necessary amount of sodium hydroxide with an agate mortar and pestle, and were used in the strength recommended by Clark with the exception of the methyl red, which was used as a 0.016 per cent solution in a 60 per cent solution of alcohol.

*Precautions.* Special emphasis must be placed upon the importance of using an agate mortar and pestle in grinding the indicators when they are to be used with slightly buffered solutions. Thus it was found that indicators ground in a glass mortar became contaminated with alkali and gave high pH values of soil solutions as is indicated in the following data:

<i>Treatment of indicator</i>	<i>pH of soil solution</i>
Indicator (brom cresol purple) ground in glass mortar.....	6.4
Indicator (brom cresol purple) ground in agate mortar.....	5.8

It was also found that upon placing 10 cc. of water in the various mortars indicated and rubbing for a minute, the conductivity water, having a pH of 5.8, changed as follows:

<i>Treatment of water</i>	<i>pH of water</i>
In agate mortar.....	5.8
In porcelain mortar.....	6.2
In glass mortar.....	7.6

The test tubes used for the buffer mixtures and for making the comparisons were thoroughly weathered by heating for  $\frac{1}{2}$  hour in dichromate cleaning solution. The following results show the effect of variously treated test tubes upon the pH of conductivity water boiled in the test tubes for 1 minute:

<i>Previous treatment of tubes</i>	<i>pH of water heated in tubes</i>
New test tubes untreated.....	6.8
New test tubes kept in boiling water for 10 hours.....	6.4
New test tubes kept in boiling 0.2 per cent HCl for 10 hours.....	6.2
New test tubes heated in dichromate solution for $\frac{1}{2}$ hr.....	5.8

The H-ion concentration of the conductivity water used was 5.8.

In these thoroughly weathered test tubes 5 cc. of the buffer solutions were placed, then sterilized, the indicators added, and the tubes sealed with paraffined corks. Made up in this manner the methyl red series of buffer mixtures was still good after 5 months. The other indicator series showed mold growth and had to be renewed after 3 months. This occurred no doubt because the indicators dissolved in water were not sterile and served to inoculate the buffer solutions, but the methyl red, dissolved in 60 per cent alcohol, was sterile and did not inoculate the buffer solution.

It was found that, in working with so slightly buffered solutions as the soil solution, great care must be taken to have the indicators absolutely neutral in reaction. To test the neutrality of the various indicator solutions used, HCl solutions of a normality to give known pH values were tested with the indicators. In some cases it was found necessary to add a little dilute HCl or NaOH to the indicators to make them perfectly neutral.

In making the comparison of the standard buffer solutions with the soil extracts or solutions, the modified Walpole comparator described by Fisher (8) was used in order to compensate for the faint yellow color of many soil solutions and extracts.

*Obtaining a clear soil extract.* After some preliminary work with centrifuged soil extracts, the method was discarded as unsatisfactory for very accurate work. In the first place, it was possible to get a clear extract only with sandy soils when a centrifuge of 1700 revolutions per minute was used. Clay or silt loams still showed considerable turbidity even after centrifuging four or five hours. Moreover, it was found that if clear extracts are centrifuged in contact with the laboratory air, their acidity decreases. Clear soil extracts were centrifuged for 2 hours in small platinum crucibles. Thus any change in reaction

could not be due to the dissolving action on glass. The following changes in reactions were found:

SOIL SOLUTION	pH VALUE BEFORE CENTRIFUGING	pH VALUE AFTER CENTRIFUGING
1	4.80	6.1
2	5.55	6.6

Centrifuging the clear soil extracts in open and closed test tubes was then tried. It was found that the soil extract of a pH value of 5.55 was not changed after centrifuging 1 hour in a closed test tube, but that in the open test tube it was changed to pH 5.8. This clearly shows that the change in reaction is due to the exposure of the solution to the laboratory air. It may be stated, also, that the centrifuge was located in a laboratory in which no chemical work was being done at the time, and which, therefore, was comparatively free from fumes.

The filter method of obtaining soil extracts was then investigated. A filtering apparatus devised by Professor E. Truog was used and found to be very satisfactory. It consists of a suction flask, a Buechner funnel, and a specially designed separatory funnel, all attached together. The separatory funnel is constructed with a wide mouth and in addition has a small side tube and stopcock attached to its neck. The Buechner funnel is fitted into the mouth of the separatory funnel with a rubber stopper and the latter placed on the suction flask with another rubber stopper. A slight suction is then applied to the suction flask, the lower stopcock of the separatory funnel being open while the stopcock on the side tube remains closed. The filter paper is placed on the Buechner funnel, wetted, and pressed down along the edges. Then, a part of the soil suspension is poured on the filter. At first the filtrate comes through turbid, but soon the soil on the filter paper forms an ultra-filter and the filtrate becomes clear. After the filtrate comes through clear, the lower stopcock of the separatory funnel is closed, and the suction removed from the suction flask to the side tube of the separatory funnel. The stopcock of the side tube is then slowly opened. By means of this apparatus it is possible to separate the first portions of the filtrate from successive portions without releasing the suction, which prevents the filter paper from rising and allowing material to get under the edges causing the filtrate to become cloudy. It also makes it possible to examine successive portions for clarity.

The filtering, of course, does not remove the slightly yellowish color of some soil extracts, but this color is compensated for by the use of the comparator already referred to. Filtering, if properly done, removes the turbidity, however, which is one of the chief sources of trouble in the color comparisons. It was found, for example, that successive portions of a certain soil extract would give a reading of pH 5.45 if allowed to filter poorly and become slightly turbid, and of pH 5.2 if the extract came through clear.

The filter paper must be free of acid or alkaline substances. Even the best

grade of ashless filter paper was found to contain some acid material. Thus, ashless filter paper with and without previous washing showed the following effects on successive portions of the soil extracts:

	FIRST PORTION	SECOND PORTION	THIRD PORTION	FOURTH PORTION	FIFTH PORTION
	pH	pH	pH	pH	pH
Unwashed filter paper.....	5.30	5.30	5.45	5.55	5.55
Washed filter paper.....	5.55	5.55	5.55	5.55	5.55

In the washing of the filter paper the following method was found very satisfactory: A dozen sheets of ashless filter paper are placed on a Buechner funnel and washed about ten to fifteen times with hot conductivity water. The filter paper is dried by placing in an oven at 50°, and is then stored in a dessicator out of contact with the laboratory air.

Care should be taken in the process of filtering not to get too much soil on the filter paper, since this necessitates the application of so much suction as to cause, with slightly buffered soil extracts, especially those near neutrality,

TABLE 1  
*Effect of aspiration of soil extracts and of conductivity water*

NUMBER	TREATMENTS OF SOLUTION	SOIL EXTRACT 1	SOIL EXTRACT 2	CONDUCTIVITY WATER
		pH	pH	pH
1	Untreated.....	6.1	4.25	5.2
2	Aspirated with ordinary air.....	6.8	4.25	5.6
3	Aspirated with air purified through soda lime....	7.6+	4.25	5.5
4	Aspirated with air purified through H <sub>2</sub> SO <sub>4</sub> .....	6.8	4.25	5.2
5	Aspirated with purified air (passed through H <sub>2</sub> SO <sub>4</sub> and soda lime).....	7.6+	4.25	5.2
6	Aspirated as in 3 and then with air purified as in 5.			5.2

high pH values. This, as will be seen from the data in table 1, is very likely due to the removal of CO<sub>2</sub> and possibly other volatile acids from the solution.

The H-ion concentrations of the extracts were determined immediately after filtering, and again after being aspirated for 15 minutes in test tubes with air treated as indicated in table 1.

It will be seen that soil extract 1 decreases in H-ion concentration when aspirated with ordinary air. This change might be due either to the removal of CO<sub>2</sub> from the solution or to the introduction of NH<sub>3</sub> from the air. If the change is due to the NH<sub>3</sub> in the air, then aspiration with air, free of NH<sub>3</sub>, should have no effect on the reaction. It is seen, however, from treatment 4, where NH<sub>3</sub>-free air was used, that the H-ion concentration also decreased to pH 6.8. Thus, the change in H-ion concentration with aspiration is due to the removal from solution of CO<sub>2</sub> and possibly other volatile acids. Treat-

ments 3 and 5 show that if air free of CO<sub>2</sub> is used, a still higher pH value is obtained. These treatments show, therefore, that this soil extract, immediately after being obtained, may be considered supersaturated with CO<sub>2</sub>; and that upon aspiration it decreases in H-ion concentration because it loses CO<sub>2</sub> and comes into equilibrium with the CO<sub>2</sub> of the air. Allowing the soil extracts to stand in a platinum crucible in contact with the air for lengths of time varying from 15 minutes and over, also resulted in a progressive decrease of the H-ion concentration of the solution which, similarly, was probably due to a loss of CO<sub>2</sub>.

Similar treatment of soil extract 2 shows that the acidity of a very acid soil extract is not affected by aspiration. This would seem to indicate that the acids giving rise to the acidity measured are not very volatile and that the extract contains sufficient acids and acid salts to be buffered against change by this treatment.

These results show, therefore, that when working with slightly acid soil extracts, care must be taken to use as little suction as possible in filtering, and to make the determinations immediately after filtering. If these precautions are not followed, the values obtained for the H-ion concentration may be low, because of a loss of CO<sub>2</sub> and possible other volatile acids.

Since the displaced soil solutions of slightly acid soils showed these same results, the same precaution against allowing them to stand must also be observed.

The effect of aspiration on conductivity water was also determined. It will be seen from treatments 2 and 3 in table 1, that the decrease of acidity upon aspiration might be due either to the removal of CO<sub>2</sub> or to the introduction of NH<sub>3</sub>. Treatment 4 shows that if NH<sub>3</sub> is removed from the aspirated air no change in pH is found. Moreover, if the water that has been raised to pH 5.5 by treatment 3, is aspirated with purified air it regains its original pH, thus proving that NH<sub>3</sub>, which had been absorbed, was removed. This shows, therefore, that conductivity water at pH 5.2 is not affected by the CO<sub>2</sub> in the air, but is readily affected by the NH<sub>3</sub> of the air. Allowing the water to stand in the air also gave it a pH value of 5.6.

#### *Comparison of the colorimetric and electrometric methods*

The H-ion concentration of a number of soils was determined by the two methods just described. In a 750-cc. Erlenmeyer flask, which had previously been well weathered, 100 gm. of soil and 200 cc. of conductivity water were placed and shaken slowly for  $\frac{1}{2}$  hour with a mechanical shaker. A portion of the suspension was then placed in the electrode vessel for an electrometric determination, and the remainder was filtered as described, and its pH value determined colorimetrically. Table 2 gives the results of the determinations by the two methods.

It will be seen that the variation between the results of the two methods ranges from + 0.1 pH to - 0.1 pH. A few soils showed greater differences,

but upon repeating, the colorimetric or the electrometric determination was found in error. It is commonly assumed, in making comparisons, that the results of electrometric determinations are standard, and differences are due to errors of the colorimetric method. The experience of the writer, however, has been that often-times upon repeating the electrometric determination, the result was found to be erroneous. This may have been due at times to a so-called "poisoned electrode."

TABLE 2  
*Comparison of the electrometric and colorimetric methods of determining the H-ion concentration of soils*

SOIL	SUSPENSION (ELECTRO- METRIC)	EXTRACT (COLORI- METRIC)	DIFFERENCE IN pH OBTAINED BY THE TWO METHODS
	pH	pH	
Reddish brown loam.....	5.81	5.75	-0.06
Light brown silt loam.....	5.78	5.80	+0.02
Light brown fine sandy loam.....	5.26	5.35	+0.09
Black silt loam.....	5.67	5.70	+0.03
	7.25	7.15	-0.10
Brown fine sandy loam.....	5.05	5.00	-0.05
Black silt loam.....	7.42	7.50	+0.08
Light brown fine sandy loam.....	5.31	5.30	-0.01
Gray fine sandy loam.....	5.57	5.60	+0.03
Brown silt loam.....	6.87	6.80	-0.07
	7.62	7.60	-0.02
	7.53	7.50	-0.03
	7.65	7.60	-0.05
Black prairie silt loam:.....	7.62	7.60	-0.02
	7.56	7.60	+0.04
	7.75	7.85	+0.10
	7.75	7.80	+0.05
	7.56	7.60	+0.04
Light colored silt loam.....	6.01	6.05	+0.04
	6.03	6.10	+0.07

The colorimetric method, therefore, can be used as a check on the electrometric method if the procedure described is followed. Since it is much simpler, requires less than a third of the time, and can be used with slightly buffered solutions like soil extracts and displaced soil solutions, it is greatly to be preferred in much of the soil work. The electrometric method is indispensable, however, in the checking up of buffer solutions and indicators.

#### HYDROGEN-ION CONCENTRATION OF THE ACTUAL SOIL SOLUTION

The question has been raised by different investigators (13), (15), (21), (25), as to whether the concentration of H-ions in the actual soil solution is obtained



by determining the H-ion concentration of the soil suspension or of the soil extract. Salter and Morgan, after a study of the effect of the soil-water ratio upon the H-ion concentration of soils, concluded from calculations that a soil at a field moisture content of 20 per cent would have an acid reaction amounting to 0.10 to 0.85 pH greater than the soil suspension at a soil-water ratio of 1:5. Thus, from a scientific as well as a practical viewpoint this question is important.

Several investigators have compared the H-ion concentration of the displaced soil solution with that of the soil suspension, and, in general, have found a higher H-ion concentration in the soil solution. Plummer (19), using the Morgan oil displacement method with application of high pressures, found that the H-ion concentration of the solution thus obtained was considerably greater than that of the soil suspension. Gimingham (12) found good agreement between the H-ion concentration of the soil solution and that of the soil suspension with some soils, but with others he got higher H-ion concentrations in the soil solution. He found that successive portions of the soil solution gradually became more turbid, and that their H-ion concentration gradually approached the value obtained with soil suspensions. Olsen (16), using a hydraulic press and considerable pressure in obtaining the soil solution, found that the soil solution was more acid by 0.1 to 0.5 pH than the soil suspension. Parker and Bryan (18) report that they found the H-ion concentration of the displaced soil solution to be "practically the same" as that of a 1:2 water extract. They do not give their results, however, nor state the number of soils upon which the comparison was made.

The varied results obtained by these investigators indicate that one or more disturbing factors were present in their determinations. Some preliminary work indicated that the manner of obtaining the soil solution may have been the disturbing factor. It is believed that the pressure method of displacement, as used by Plummer and Olsen, may not give the actual or unchanged soil solution.

#### *Obtaining the soil solution*

In the present investigation the displacement method described by Parker (17), with modifications as herein described, was used. The glass percolators had a capacity of about eight to nine hundred grams of soil.

Since the time for displacement of 10-cc. portions, the amount used for the test, would usually take about an hour, it seemed necessary to protect the displaced solution from the laboratory air and prevent it from losing any  $\text{CO}_2$  that it might contain. This was done by means of a 10-cc. pipette which had its tip cut off and the upper part bent back in the shape of a U. One end was placed in the hole of the rubber stopper of the percolator, and the displaced solution was thus collected with a minimum amount of contact with the laboratory air.

After some preliminary work it became apparent that the iodoform test used by Parker for testing the appearance of very small amounts of alcohol in the

displaced solution was unsatisfactory. Since the presence of a very small amount of the displacing solution would naturally affect the H-ion concentration of the displaced soil solution, the need of getting a very sensitive test for the first appearance of the displacing solution seemed important. The need was felt even more greatly in further work where displacements of soil solutions from soils treated with carbon dioxide were investigated. The use of potassium thiocyanate was finally adopted. Theoretically, it should be very satisfactory, for most of the thiocyanates are soluble and therefore would not be removed from solution while passing through the soil column. Moreover, the presence of thiocyanate can be detected in very small quantities. Thus it was found that the characteristic red color is obtained when 5 cc. of a 0.005

TABLE 3

*The presence of thiocyanates in successive portions of the displaced soil solution and its relation to total salts and pH values*

PORTION	TIME, AFTER STARTING DISPLACE- MENT, OF COLLECTION OF PORTIONS	TOTAL SALTS BEFORE IGNITION IN 5-CC.* SAMPLES	pH	TEST FOR PRESENCE OF CNS
	<i>hours</i>	<i>gram</i>		
1	4½	0.0068	6.65	—
2	5½	0.0062	6.65	—
3	6½	0.0062	6.65	—
4	7½	0.0065	6.65	+
6†	29	0.0060	6.75	+
8	31	0.0075	6.50	+
9	32	0.0108	6.20	+
10	33	0.0138	6.00	+

\* Ten-cubic centimeters portions were collected each time but only 5 cc. was used for the determination of total salts.

† Displacement was stopped over night.

per cent solution is tested with a drop of ferric chloride. A 0.5 per cent solution was used for displacement. Thus if a drop of the displacing solution were present in 5 cc. of the displaced solution, it could be detected.

The data in table 3 indicate that the test is adaptable to the work. It is to be noted that a test for thiocyanate may be obtained before there is a change in the H-ion concentration or in the total salts. This indicates the extreme sensitiveness of the test. The table also shows the usual time taken for displacement. The soil used was a Miami silt loam with a moisture content of 16 per cent. The total amount of soil used was 810 gm. Thus the percentage displacement of the total water present, before a test for thiocyanate was obtained was 22.7 per cent, and before the total salts changed, 53 per cent.

An effort was made to obtain by the use of additional small amounts of pressure a shorter time of displacement. It was found, however, that if pressure is used, a harder packing of the soil becomes necessary in order to get good displacement, and thus the time of displacement is not shortened. Water and

50 per cent alcohol were compared for displacing the soil solution. It was found that the alcohol solution gave a greater total displacement, but that the displacement took longer than with water. In most of the work, therefore, water was used, for it seemed more essential to get a quick displacement than to get a greater total displacement.

*Comparisons of the H-ion concentrations of soil solutions and of soil suspensions*

The soils used for displacement were taken from the field late in the fall and kept in a cool greenhouse all winter in large cans which were covered so as to maintain the soils at constant moisture content. Table 4 gives data which make possible a comparison between the H-ion concentrations of the soil solution, the soil suspension, and the soil extract. It will be noticed that, contrary to the results of most investigators, the soil solution is not at a higher H-ion concentration than the soil suspension or soil extract. It seems probable that

TABLE 4  
*The H-ion concentrations of soil solutions, soil suspensions, and soil extracts*

SOIL	DISPLACED SOIL SOLUTION	SOIL SUSPENSION	FILTERED SOIL EXTRACT
	pH	pH	pH
Brown silt loam.....	5.65	5.54	5.60
Brown fine sandy loam.....	5.55	5.57	5.60
Brown silt loam.....	5.25	5.19	5.20
Black silt loam.....	7.90	8.01	7.95
	7.50	....*	7.50
Light brown silt loam.....	6.80	6.85	6.80
Brown silt loam.....	4.40	....*	4.25

\* Not determined.

the failure to get agreement between the H-ion concentration of soil solutions and soil extracts or suspensions by the various workers, whose works have been cited, is due to the fact that they did not obtain the actual soil solution. The experience of the writer has been that with many soils the use of much pressure in obtaining the displaced soil solution makes it difficult, even with the most careful packing, to get the first portion of the displaced soil solution uncontaminated with the displacing solution.

It is evident from these data, therefore, that the determination of the H-ion concentration of soil suspensions or of soil extracts gives the reaction of the soil solution. The further significance of these data will be discussed later in relation to the effect of the soil-water ratio on the H-ion concentration.

EFFECT OF CO<sub>2</sub> ON THE H-ION CONCENTRATION OF SOILS

It might be argued, however, that the soils used in the previous experiments contained little CO<sub>2</sub> and that under field conditions where plants are growing,

differences in H-ion concentrations may exist because of the  $\text{CO}_2$  present. As is generally known, rather large amounts of  $\text{CO}_2$  are produced by plant roots, decomposing organic matter, and bacteria in the soil. Stoklasa (24) calculated that in a hectare of soil 75 kgms. of  $\text{CO}_2$  are given off by bacteria, and about 60 kgms. by plant roots daily. The question exists, whether the  $\text{CO}_2$  present in field soils affects the soil reaction.

Olsen (16) in his investigations found that some plants that thrive well on alkali soils make poor growth in nutrient solutions of similar alkaline reaction. He concludes, therefore, that plants on an alkali soil are actually growing in a more acid solution than is indicated by the determination of the H-ion concentration of the soil suspension, and that this more acid reaction is due to the  $\text{CO}_2$  excreted by the plant roots.

#### *Effect of the $\text{CO}_2$ given off by growing plant roots*

In order to determine the effect of the  $\text{CO}_2$  present in the soil under field conditions, the soil solutions from soils on which barley and rye plants were actively growing were obtained by the displacement method. At the same time soil solutions were obtained from uncropped portions of these same soils. No difference was found between the H-ion concentrations of the displaced solutions of cropped and of uncropped soils. Both acid and alkaline soils were used in this comparison. It is possible, however, that, in packing the soil for displacement, the  $\text{CO}_2$  of the soil air might diffuse out, even though the time of packing never exceeded two or three minutes. The  $\text{CO}_2$  in the soil may also be more concentrated in the thin film around the root hairs and thus exert a greater action there than at other points in this thin layer, although not affecting the whole soil solution. Further work along this line was, therefore, believed necessary.

#### *Effect of introducing a stream of $\text{CO}_2$ into soil suspensions during electrometric determinations*

In studying this problem, Sharp and Hoagland (22) determined the effect of adding varying amounts of  $\text{CO}_2$  on the H-ion concentration of soil suspensions. They found that a  $\text{CO}_2$  content of 10 per cent of the gas mixture introduced into the electrode vessel had little effect on the H-ion concentration of acid soil suspensions. With neutral soils, however, they obtained a slight increase in the H-ion concentration, and with strongly alkaline soils, a decided increase. They believe, however, that the small amount of  $\text{CO}_2$  found in the soil air is insufficient to produce a change in the reaction of the soil solution.

In a similar manner, the writer determined the H-ion concentration of soil suspensions electrometrically before and after the addition of  $\text{CO}_2$ . The  $\text{CO}_2$  was introduced by passing it in from the bottom of the electrode vessel and allowing it to saturate the soil suspension. The hydrogen was introduced from the top only.

Table 5 shows that the passage of CO<sub>2</sub> through the soil suspensions increased the H-ion concentration of both acid and alkaline soils. It will be noticed that alkaline soil suspensions are made slightly acid and that this acid reaction is much the same for all the alkaline soils, regardless of their original H-ion concentration. With acid soil suspensions also, after being saturated with CO<sub>2</sub> a similar value is obtained. The equilibrium thus reached for the alkaline soils is no doubt due to the CaCO<sub>3</sub>, but with the acid soils other salts are concerned. This seems to be indicated by the work of Shipley and McHaffie (23) on water solutions. They found that a solution of CaCO<sub>3</sub> with a H-ion concentration of pH 9.4 gave a reaction of pH 6.56 when saturated with CO<sub>2</sub>, and a solution of CaSO<sub>4</sub> plus CaCO<sub>3</sub> gave a pH value of 5.11 when similarly treated.

Although these data would seem to indicate that the CO<sub>2</sub> of the soil may affect the soil reaction, it is evident that a much higher amount of CO<sub>2</sub> was used here than is found under field conditions, and that field soils would natu-

TABLE 5  
*The pH values of soil suspensions with and without the introduction of CO<sub>2</sub>*

SOIL	SOIL SUSPENSION (ELECTROMETRIC)	
	Before adding CO <sub>2</sub>	After adding CO <sub>2</sub>
	pH	pH
Black prairie silt loam.....	5.54	4.84
	7.64	6.45
Brown fine sandy loam.....	5.57	4.81
	5.22	4.72
Brown sandy loam.....	9.62	6.19
Black silt loam.....	8.04	6.15

rally be much better buffered than are soil suspensions. It is also possible that in these determinations the H-ion concentrations may be affected by the saturation of the solution with CO<sub>2</sub> and the lessened hydrogen pressure.

*Effect of introducing CO<sub>2</sub> into the soil before displacement of soil solution*

In order to approach more closely field conditions and to eliminate the possible sources of error just mentioned, the soil was packed in the percolator as for displacement, and CO<sub>2</sub> introduced from a tank. The percolator was closed on top with a rubber stopper and the CO<sub>2</sub> introduced through a tube in the stopper at a rate of about 30 to 50 bubbles per minute for about a half hour. The bottom and top of the percolator was then closed and the CO<sub>2</sub> allowed to come into equilibrium with the soil by allowing the percolators to stand in that manner for 1 hour before displacement was begun.

It was found that this slow passage of CO<sub>2</sub> into the soil would not cause air channels to be formed, and, therefore, repacking in another percolator was unnecessary to get good displacement. This removed the objection previously raised that in the process of packing, the CO<sub>2</sub> may be lost from the soil.

The data in table 6 show that, with the exception of the brown silt loam, the passage of  $\text{CO}_2$  through the soils does not affect the H-ion concentration of the displaced soil solutions. This brown silt loam shows a more alkaline reaction upon treatment with  $\text{CO}_2$ , which would seem to indicate that in this case the  $\text{CO}_2$  had brought basic material into solution. The displaced solution from the limed quartz sand, however, shows a much higher H-ion concentration after treatment of the sand with  $\text{CO}_2$ . This may be explained by the fact that the sand is only very slightly buffered, and thus would be easily affected.

It seems very probable, therefore, that because of the buffer capacity of the soil, the  $\text{CO}_2$  secreted by plant roots and given off by bacteria in the soil has little effect on the H-ion concentration of the soil solution as a whole. It is possible, however, that the film of moisture in direct contact with the root hairs may be slightly affected by a high concentration of  $\text{CO}_2$  arising from that

TABLE 6  
*The H-ion concentration of displaced soil solutions of untreated soils and of the same soils treated with  $\text{CO}_2$*

SOIL	DISPLACED SOIL SOLUTION FROM UNTREATED SOIL	DISPLACED SOIL SOLUTION FROM $\text{CO}_2$ -TREATED SOIL
	pH	pH
Brown fine sandy loam.....	6.70	6.70
Brown silt loam.....	6.55	6.80
Dark brown silt loam.....	5.55	5.45
Black silt loam.....	7.40	7.40
Light brown sand.....	5.30	5.30
Brown fine sandy loam.....	5.60	5.70
Limed quartz sand.....	7.60	5.70

excreted by the root hairs. Thus, there may be small local areas of soil solution about the root hairs that have a slightly greater acidity than the remainder of the soil solution.

#### EFFECT OF THE SOIL-WATER RATIO ON THE H-ION CONCENTRATION

If the ratio of soil to water affects the H-ion concentration, it would seem reasonable to believe that the reaction of the actual soil solution would be different from that of the soil suspension at a soil-water ratio of 1:2, for the amount of water in contact with a definite amount of soil is about ten times as much in the latter case. It has been shown in table 4 that there is no significant difference between the reaction of the actual soil solution and a soil suspension. Various investigators, however, working with higher dilutions of the soil suspension, have obtained conflicting results; and those that have obtained differences, as the soil-water ratio varied, have contended that an acid condition of the soil solution is due to adsorption and not to insoluble or slightly soluble acids and acid silicates. From a theoretical viewpoint, therefore, this question becomes of fundamental importance.



Sharp and Hoagland (21), on the one hand, found no significant differences in the H-ion concentration of soils at soil-water ratios varying from 1:2 to 1:500. Although with one soil they report a more acid reaction amounting to about 0.7 pH with the higher soil-water ratio, they state that the differences obtained are most likely due to limitations of the electrometric method. Gillespie and Hurst (11) found no consistent differences in the H-ion concentration of soil extracts, determined by the colorimetric method, using soil-water ratios of 1:1 and 1:2. Their results vary from  $-0.15$  to  $+0.25$  pH, based on the 1:1 as a standard. Arrhenius (1) reports work on two soils and believes that the change in H-ion concentration with different soil-water ratios is dependent on the kind of soil. Thus he found little change with a humus-rich soil, but a change of 0.9 pH with a sandy soil, when ratios of 1:2½ and 1:500 were compared. Bradfield (2), also using the H-electrode, found that the colloidal portion of an acid clay showed no significant difference in H-ion concentration when the soil-water ratios were varied from 1:8 to 1:34. With lower soil-water ratios, however, he found that the H-ion concentration decreased with dilution.

On the other hand, Salter and Morgan (20) found an increase in H-ion concentrations with an increase in the soil-water ratio of all the soils studied. Thus between a soil-water ratio of 1:1 and one of 1:25, they found differences on 9 soils varying from 0.33 to 0.95 pH. Still higher ratios of water to soil showed the same relation. These investigators used the electrometric method.

A further discussion of the results just reviewed and their relation to the nature of soil acidity is given on pages 301 and 302.

After some preliminary work with the H-electrode on soil suspensions at different dilutions or soil-water ratios,<sup>2</sup> it was found that increasing the dilution usually decreased the H-ion concentration. This is in accordance with the work of Salter and Morgan. The results, however, were very inconsistent at high dilutions, and it was thought that possibly the dilution so reduced the buffer action of the suspension as to make electrometric determinations at these lower soil-water ratios unreliable.

The colorimetric method was, therefore, used in the following work. Paraffined flasks were used in making the soil suspension, in order to prevent any contamination from the glass, which is possible especially when working with low soil-water ratios.

The filtering was done as previously described, except that with high dilutions just sufficient suction was used to keep the filter paper well pressed against the funnel. A smaller Buechner funnel, having a filtering surface of about one inch in diameter, was used. It was found that a very thin layer of soil was sufficient to act as an ultra-filter. Little difficulty was encountered in getting clear filtrates.

With most of the soils, the ratios of 1:2 and 1:50 were used. The difference between these two ratios was believed to be sufficient to prove or disprove the

<sup>2</sup> The term *high dilution* is used synonymously with *low soil-water ratio*.

point in question, for differences in H-ion concentration as high as 1.0 pH between these two ratios were found by Salter and Morgan. It is believed that when extremely high ratios are used, the solution becomes so slightly buffered as to be affected easily by the purity of the water or other factors. This seems to be indicated by the work of Bradfield.

TABLE 7  
*The H-ion concentration of soils as affected by the soil-water ratio and previous washing*

SOIL	TREATMENT	SOIL EXTRACTS AT SOIL-WATER RATIOS OF		
		1:2	1:20	1:50
		pH	pH	pH
Light brown silt loam.....	None	4.25	....*	4.80
	Washed	5.00	....*	5.00
Reddish brown fine sandy loam.....	None	4.95	5.25	5.45
	Washed	5.45	5.45	5.45
Black sandy loam.....	None	4.50	....*	5.05
	Washed	5.10	5.20	5.20
Red clay.....	None	5.00	....*	5.20
	Washed	5.40	....*	5.40
Poorly decomposed peat.....	None	3.65	4.30	4.80
	Washed	5.20	....*	5.30
Brown fine sandy loam.....	None	5.60	5.70	5.60
Black silt loam.....	None	5.55	5.55	5.55
	None	7.80	7.80	7.80
Gray fine sandy loam.....	None	5.65	5.65	5.65
Brown silt loam.....	None	6.10	....*	6.10
Light brown silt loam.....	None	6.05	....*	6.05

\* Not determined.

Table 7 shows that the H-ion concentrations of some soils vary with the soil-water ratio, although other soils show no differences. It also appears from the data of the soils studied that the most acid soils are those most affected by changing the soil-water ratio, and that this relation seems to hold regardless of the texture of the soil. This latter fact would seem to indicate that a change with different soil-water ratios is not confined to soils that are slightly buffered, as was suggested by Arrhenius. Another explanation for the change in H-ion concentration of soils as a result of dilution is therefore needed. It is

generally recognized that soluble salts are present in soils, and it is evident that they would affect the H-ion concentration. Moreover, in acid soils there is found in addition to the insoluble acids a small amount of soluble acids. Upon dilution of the soil with water, then, it follows that the concentrations of the soluble salts and the more soluble acids would be decreased and the H-ion concentrations would thus also be decreased.

In order to establish this point, 100 gm. of those soils, which showed a difference in pH on dilution, were thoroughly washed on a Buechner funnel with about twenty successive portions of 100 cc. of conductivity water during a period of about ten hours. Since most of the soluble salts and soluble acids are thus washed out, the washed soils should show no difference in H-ion concentration with different soil-water ratios. An examination of table 7 will show that this was found to hold true. These results are, therefore, in agreement with those previously obtained in comparing the H-ion concentration of soil solutions with that of soil suspensions. They show that where the insoluble acids are alone or mainly responsible for the acidity of the soil, no change occurs with the use of different soil-water ratios. The conflicting results reported by various investigators may thus be explained.

#### NATURE OF SOIL ACIDITY AS REVEALED BY THE H-ION CONCENTRATION OF SOILS AT DIFFERENT SOIL-WATER RATIOS

Much work has been done in recent years in an attempt to explain the nature of soil acidity. It does not seem necessary to review the literature of this vast subject here, for good résumés of the subject have been made by Truog (27), Fisher (8), Sharp and Hoagland (21) and others. It is sufficient to state that at the present time two main theories as to the nature of soil acidity are being supported by different investigators. These are the mineral acid theory and the selective adsorption theory.

Of these two theories, the mineral acid theory seems to have received, recently, the greatest amount of support as a result of the work of Truog, Gillespie, Sharp and Hoagland, and Bradfield.

Salter and Morgan, however, in the work previously cited on the effect of the soil-water ratio on the H-ion concentration, obtained data which they interpreted as supporting the adsorption theory of soil acidity. They argue that if soil acidity is due to insoluble acids present in the mineral portions of the soil, the same H-ion concentration should be obtained at different soil-water ratios, since with all ratios used a saturated solution of the relatively insoluble mineral acids would be present. Since they find decreases in the H-ion concentration with decreased soil-water ratios, and since the relation between the H-ion concentration and the soil-water ratio seems to follow an adsorption curve, they believe that they are dealing with an adsorptive phenomenon or that soil acidity is at least partially of an adsorptive nature.

Bradfield interprets the data of Salter and Morgan as supporting the presence of colloidal mineral acids. He maintains that it cannot be assumed that

an excess of insoluble acids is present at all soil-water ratios even though some soil particles are present. As has already been mentioned, Bradfield worked with a colloidal extract of an acid clay, and found little difference in the H-ion concentration with soil-water ratios ranging from 1:8 to 1:33, but found a decrease in H-ion concentration with lower ratios of soil to water. He shows, however, that the curve which expresses this relationship is also characteristic of such acids as acetic acid, and therefore concludes that the curves offer no proof that the phenomenon in question is adsorptive.

The investigators just mentioned used in their work the H-electrode, which is not suitable for use with slightly buffered solutions. Since the soil suspension becomes slightly buffered upon high dilution, it seems probable that the differences in H-ion concentration that these investigators obtained with low soil-water ratios may be due to limitations of the electrometric method.

The results reported in table 7 show that if the colorimetric method is used in determining the H-ion concentration, no differences are obtained with some soils at different soil-water ratios. Where differences were obtained between the H-ion concentrations of a soil at different soil-water ratios, they were found to be due to the presence of soluble salts and acids. It is evident, therefore, that soil acidity is due primarily to the presence of mineral acids in the soil. Varying the soil-water ratio within wide limits gives solutions that are saturated with respect to the relatively insoluble soil acids and, therefore, give the same H-ion concentration. It is unnecessary, therefore, to resort to an adsorption theory to explain the nature of soil acidity which at best is very hard to understand or explain.

#### SUMMARY

A study was made of the effect of carbonic acid and the soil-water ratio on the H-ion concentration of soils. In the preliminary work it was found necessary to make a study of methods with special reference to the factors affecting the accuracy of the colorimetric method. The H-ion concentrations of soil suspensions determined by the electrometric method and of filtered soil extracts and displaced soil solutions determined by the colorimetric method were compared. Carbon dioxide was passed through soil suspensions and the change in the H-ion concentration of the suspensions was determined. A study was then made of the possible effect of  $\text{CO}_2$  found in soils upon the H-ion concentration of the actual soil solution. This was done by comparing the H-ion concentration of the displaced soil solution from a soil in which plants were actively growing with that from the same soil kept bare. In addition,  $\text{CO}_2$  was passed through soils and the effect on the H-ion concentration of the displaced solution noted. The H-ion concentrations of soils at soil-water ratios of 1:2 and 1:50 were determined. Where differences in the reactions were obtained with different soil-water ratios, the soils were washed to get rid of the soluble salts and the more soluble acids, and the effect of using different soil-water ratios was again determined. The data obtained in these studies

are discussed as regards their relation to the nature of soil acidity. The results may be summarized as follows:

#### *Methods*

1. The electrometric method of determining the H-ion concentration is unsuitable for such slightly buffered solutions as soil extracts and soil solutions.

2. The colorimetric method was found to be convenient and accurate for determining the H-ion concentration of filtered soil extracts and soil solutions, provided certain precautions are observed, as follows:

a. The soil extract must be perfectly clear.

b. Clarification of soil extracts can be accomplished best by filtering. It is necessary to use thoroughly washed filter paper and special suction apparatus, as described. The centrifugal method does not clarify all soil extracts, and, moreover, the containers must be stoppered during centrifuging; otherwise the acidity of the solutions is usually decreased because of exposure to the laboratory air.

c. The H-ion concentration of the filtered soil extracts and of the displaced soil solution must be determined immediately after the solutions are obtained because of change of reaction upon standing.

d. The test tubes and glassware used must be thoroughly weathered.

e. The indicators must be neutral in reaction. If it is necessary to grind them before solution, glass or porcelain mortars should never be used, for they contaminate the indicator by making it alkaline. An agate mortar and pestle may be used.

3. In obtaining the soil solution, the displacement method described by Parker was used. It was found that an accurate test for the first appearance of the displacing solution in the displaced soil solution was necessary, because the presence of small amounts of the displacing solution greatly affected the H-ion concentration of the displaced soil solution. A sensitive test involving the use of KCNS is described.

4. Filtered soil extracts, soil suspensions, and displaced soil solutions were found to give the same H-ion concentration.

#### *Effect of carbonic acid*

1. If during the electrometric determination, CO<sub>2</sub> is conducted into a soil suspension from the bottom of the electrode vessel while the hydrogen is introduced only from the top, the CO<sub>2</sub> causes an increase in H-ion concentration.

2. The displaced soil solutions from either acid or alkaline soils upon which plants are actively growing and giving off CO<sub>2</sub> were found to have the same H-ion concentration as corresponding uncropped soils.

3. The passage of CO<sub>2</sub> through the soil does not affect the H-ion concentration of the displaced soil solution. Similar treatment of a limed quartz sand greatly increased the H-ion concentration of the displaced solution. This shows that soils are strongly buffered to CO<sub>2</sub>, and indicates that the H-ion concentration of the actual soil solution is probably not affected to any important extent by the CO<sub>2</sub> given off by plant roots and decomposing organic matter.

*Effect of the soil-water ratio and the nature of soil acidity*

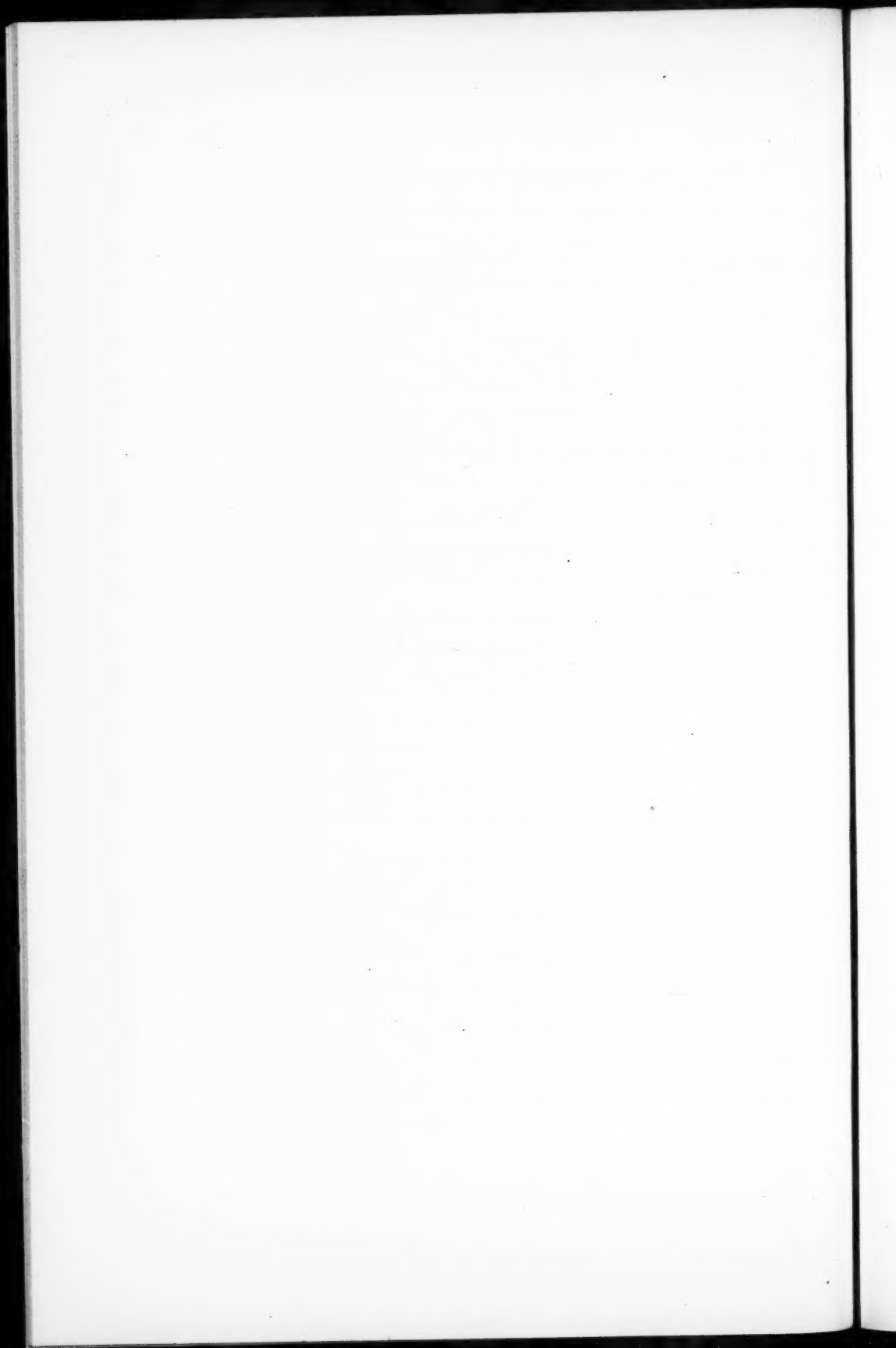
1. The H-ion concentrations of some soils are not affected by changing the soil-water ratio from 1:2 to 1:50.
2. Soils that show a change in H-ion concentration with different soil-water ratios no longer show such differences after soluble salts and the more soluble acids are washed out. After washing, the acidity of the soil is due entirely to the relatively insoluble acids.
3. The data obtained on the effect of the soil-water ratio support the mineral acid theory of soil acidity. Under conditions of equilibrium the solution in contact with the soil becomes saturated with respect to the relatively insoluble soil acids. Therefore, as long as some of these acids are present undissolved, the H-ion concentration is the same for different soil-water ratios. An explanation of the nature of soil acidity by means of the adsorption theory is, therefore, unnecessary.

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## A CRITICAL pH FOR THE FORMATION OF HARDPAN IN ACID CLAY SOILS

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Work done in the summer of 1923 on an area of ground situated near the campus of the University of Pennsylvania, in Philadelphia, suggested that several apparently diverse soil factors were dependent one upon the other. Subsequent experiments on the adsorption of many ions by kaolin and the effect of these ions on the charge of the kaolin particles, indicated that pH is dependent on the salt content of the soil which, in turn, affects the size of the soil aggregates to a marked extent. As these latter data are incomplete this paper confines itself to the presentation of some evidence in support of the view that there is a definite pH at which hardpan is formed in acid clay soils, above which it cannot be formed, and below which it may appear.<sup>1</sup>

By "hardpan" is here meant that stratum found at varying depths below the soil surface composed of "clays" and sand more or less cemented by precipitated Fe, Al, and sometimes organic compounds. Such a partial definition eliminates the alkali hardpans of the West, the mechanical hardpans of certain soils in Florida and Bermuda, and "plow sole."

The area above referred to is bounded on the south by the Schuylkill River upon whose opposite banks are situated a large number of industries and railroads. Smoke is produced in great quantities and is blown over the area by the prevailing winds. The northern boundary is about fifteen hundred feet from the river where begins a residential district. Gardeners were unable to get the usual grass mixtures to grow at all on the southern portion, although the northern part produced a fair turf. It was believed that an extreme acidity of the soil was produced by the  $\text{SO}_2$  and its derivatives blown from the railroads and factories and deposited for the most part on the southern part of the area in question. Proof of this theory was sought.

At 160 stations, pH values were obtained at depths of 6, 12 and 18 inches. Samples of the soil were obtained by means of a soil auger graduated at the three levels. The pH values were determined in the laboratory by means of a comparator copied for the most part after Van Alstine (1), brom-phenol-blue and brom-cresol-purple being used as indicators. Results so obtained were checked on the potentiometer using the dip electrode. Brom-phenol-blue

<sup>1</sup> Thanks are due Dr. Rodney H. True and Dr. Merkel Jacobs for their help and suggestions in this work.

checked within  $\pm 0.1$  pH with the potentiometer and brom-cresol-purple agreed within limits of  $\pm 0.15$  pH. Methyl red proved entirely unreliable, and at that time brom-cresol-green was not advocated.

In making borings with the auger, it was noticed that hardpan was present in some places while entirely absent in others in the same general area. Then, too, it was found at varying depths. The water content of the soil varied from a saturated condition in some places to a desiccated condition in others. The degree of hardpan and the approximate percentage of water were noted in all cases. The degree of water present was based on the saturated condition of the soil as 100 per cent.

Only such data are presented as apparently bear on the formation of hardpan. Thus only those determinations made within a circle of 400-foot radius, tangent to the southernmost boundary of the area are used. These are summarized in table 1.

Generally speaking, it may be said that the pH increased and the hardpan decreased with the distance from the railroads and factories. At some locations, hardpan occurred with a pH as high as 5.2 and was absent at a pH of 4.7. However, such cases were the exception and probably may be explained on

TABLE 1  
*Summary of pH, hardpan, and water determinations at 3 levels*

DEGREE OF HARDPAN	NUMBER OF DETERMINATIONS	AVERAGE WATER	NUMBER OF DETERMINATIONS	AVERAGE pH	NUMBER OF DETERMINATIONS	AVERAGE pH	NUMBER OF DETERMINATIONS	AVERAGE pH
		<i>per cent</i>		<i>6 inches</i>		<i>12 inches</i>		<i>18 inches</i>
Well defined.....	15	40	14	4.75	15	4.75	14	4.70
Slight.....	30	50	28	4.85	28	4.85	26	4.95
None.....	23	75	23	4.95	21	5.15	19	4.85

the basis of the salt content of the soil. In no case was a hardpan layer found at a depth less than ten inches and rarely occurred further from the surface than fifteen inches. Where hardpan was well defined, the soil above the layer was very dry although below the layer the soil was in most cases nearly saturated with water. The pH of the the soil above the layer was, as a rule, from 0.2 to 0.5 lower than that of the soil below the layer.

These data indicate that with this heavy clay soil, there is a certain pH (about  $4.8 \pm 0.1$ ) at which a hardpan layer will be found, above which it is not found, and below which it is either well defined or absent.

Insofar as the hardpans encountered in the field work were cemented by Fe and Al for the most part (silica sols were also a factor in the cementing but were apparently cemented and precipitated by the heavy metals) the following experiments were devised to show that  $\text{Fe}(\text{OH})_3$  may be precipitated on kaolin, resulting in a "hardpan" analogous in many physical respects to that found in the field. The pH at which approximately all the Fe is precipitated and the maximum flocculation of the kaolin particles occurs is just above that pH at which hardpan was found in the field.

Fe was used in all cases because of the ease with which its changes may be observed. Al could have been used but would have involved quantitative analyses and would not have made results so clear as Fe.

A. The base of a graduated liter cylinder was connected to a suction pump creating a pressure of three-quarters of an atmosphere. The connection was covered with glass wool and a thin layer of cotton. Then 500 cc. of a mixture of Merck's kaolin, Juniata crushed quartz and  $\text{CaCO}_3$  was packed into the cylinder. The quartz was added to permit the easy passage of water, and the  $\text{CaCO}_3$  to insure a high pH.  $\text{FeCl}_3$  was mixed with sand and kaolin and 100 cc. was packed above the preceding mixture. The cylinder was then nearly filled with sand and kaolin. The suction was applied and 0.001 *M*  $\text{H}_2\text{SO}_4$  drawn through. The dilute acid passed quickly down the "soil" until it came to the 500 cc. mark where a dull red layer of Fe was precipitated. This layer was found exactly where the mixture containing Fe and Ca joined, and prevented the passage of water downward for upwards of fifteen minutes. Then a breach was made in the eighth-inch red layer and the liquid thus released washed a channel to the bottom of the cylinder. Aggregates of sand and kaolin colored slightly yellow with  $\text{FeCl}_3$  were carried down from the Fe layer, and where such aggregates came in contact with  $\text{CaCO}_3$  they immediately turned dull red and adhered to the sides of the channel. The final result was a broken, dull red layer at the 500 cc. mark and an irregular channel extending to the bottom of the cylinder, least red at the base and most red at the point of origin. The rest of the "soil" remained colorless.

This experiment does not purport the reproducing of a soil condition as one finds it in the field. It suggests only the binding action of precipitated Fe on sand and kaolin particles and, which is more important, that this binding effect forms a layer which is impervious to water even under a pressure of 12 pounds. It throws some light on the very peculiar stratifications found in some soils.

B. The above experiment was repeated, differing only in the elimination of  $\text{CaCO}_3$ . No precipitate of any kind was discernible.

C. The following experiment is similar to A but attempts to show that the red layer described is formed only at that pH precipitating Fe.

A number of U-tubes with a length of leg of 4 inches and a diameter of 1 inch were filled at the base of the U with a mixture of sand, kaolin and  $\text{FeCl}_3$  and saturated with water (mixture A). The legs were filled with sand and kaolin (mixture B). One leg of each tube was immersed in a concentrated NaOH solution and the other in a concentrated HCl solution. The base of each U-tube had a slight yellow color whereas the remainder was colorless. At the end of 2 weeks a faint red color was apparent at the point where mixtures A and B met. This red color slowly spread upward and blended with the yellow color about one inch from the point of origin. This occurred in the leg of the U-tube immersed in the NaOH. About a week later, the red was well defined on the alkaline side but no change was apparent on the

acid. The experiment was continued a month longer with no significant change.

D. The same experiment was repeated with a heavy clay soil which was obtained in the field and which showed a high Fe content. The pH of this soil was adjusted to 4.5. In several weeks a decided red layer was precipitated in the leg of the U-tube immersed in the NaOH, but no change was noticed in the leg influenced by HCl.

The red layers were found to be impermeable to water subjected to a pressure, were compact, and when dry, brittle. Dissolved by HCl, the red color disappeared and water again passed through.

E. To each of 6 test tubes 10 gm. of air-dry kaolin was added. To 4 of the tubes were added 1 gm. of  $\text{FeCl}_3$  and various amounts of NaOH as indicated by table 2. The tubes were then stoppered, well shaken and allowed to settle. A sample from each tube was diluted so that the resulting solutions were equivalent to 0.02 N Fe. Determinations were then made for pH, using the Cornel modification of the dip electrode.

TABLE 2  
*Precipitation of Fe at various pH values*

	TUBE 1*	TUBE 2*	TUBE 3*	TUBE 4*	TUBE 5*	TUBE 6
		NaOH $\rightleftharpoons$ 5.15 cc. normal	NaOH $\rightleftharpoons$ 7.73 cc. normal	NaOH $\rightleftharpoons$ 9.03 cc. normal	NaOH $\rightleftharpoons$ 10.33 cc. normal	
Supernatant liquid.....	Yellow	Brown yellow	Red brown	Turbid	Clear	Clear
Sediment.....	Yellow	Brown	Darker than 2	Darker than 3	Darker than 4	White
pH.....	3.4	3.6	4.4	5.0	5.6	5.5

\* Containing, in addition to the kaolin,  $\text{FeCl}_3 \rightleftharpoons$  18.48 cc. normal.

Practically all the Fe was precipitated in tube 4, and apparently most was present in tube 3 as the OH, so that as demonstrated in the pH determinations, a slight increase in the pH resulted in the rapid precipitation of the Fe as the OH. Considerable difficulty was experienced in obtaining the pH values; many determinations were made and variations from the averages recorded in the table were  $\pm 0.2$  pH. Such results are sufficiently accurate for the present consideration. It will be noted then, that Fe is entirely precipitated at pH values slightly above 5.0, and is, if adsorption be disregarded, entirely in solution at pH values of about 4.4. It should be possible, therefore, to cement a hardpan in the soil at any pH between approximately something above 4.4 and below 5.0. This consideration, it will be noted, refers only to Fe and Al as cementing agents in the formation of an impermeable layer. The hardpans encountered in the field work before described were present at pH values of from 4.70 to 4.95; slight at the latter values and well marked at the former.



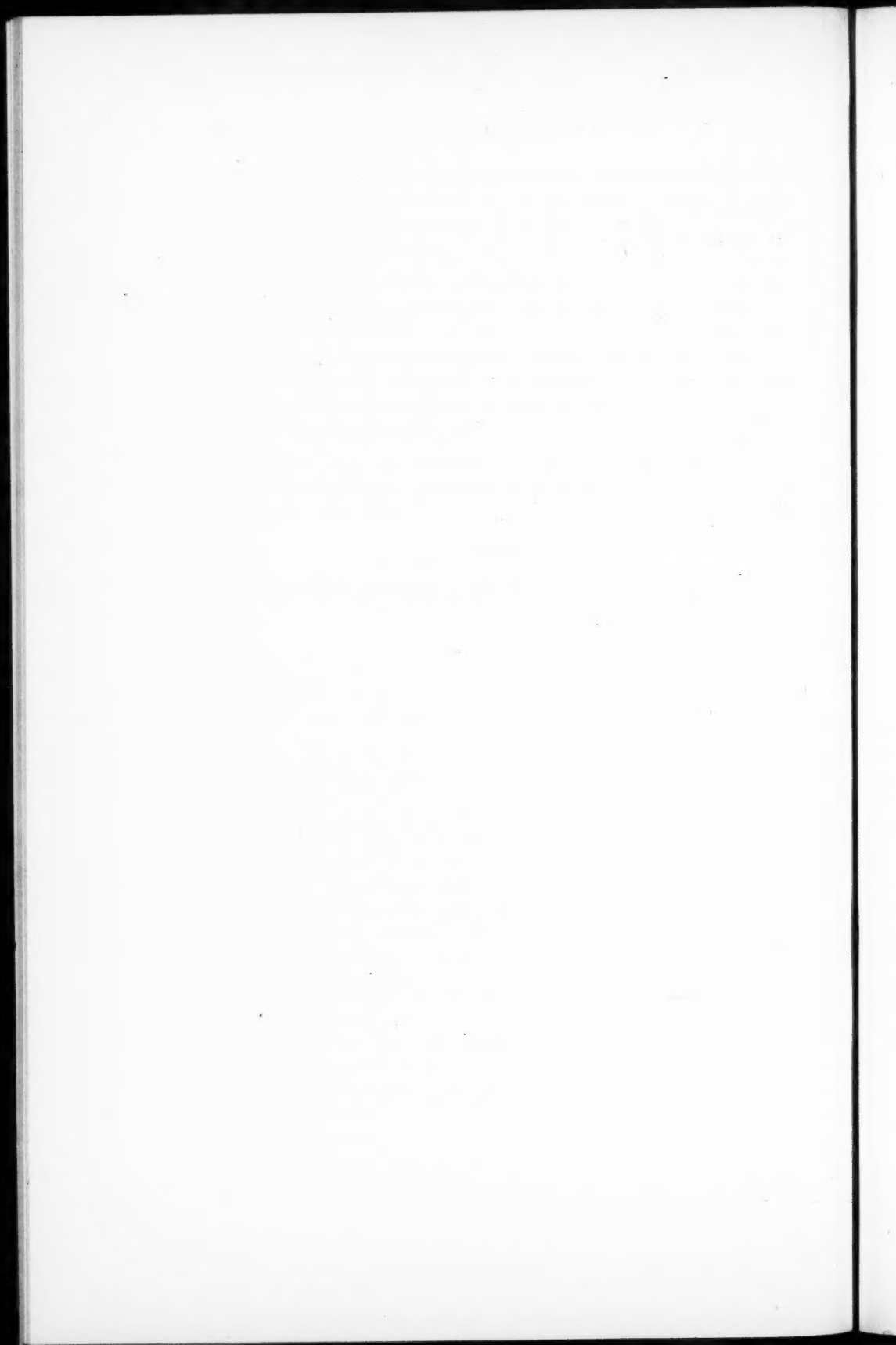
Any explanation of these observations seems to require an understanding of the adsorption of various ions by clay particles and the effects of such adsorption on the particles. A number of such studies have been made but the data are too incomplete to present at this time.

#### SUMMARY

1. Hardpans observed in the field were present in acid clay soils from pH 4.70 to pH 4.95.
2. "Hardpans" having generally the same physical properties as those occurring naturally were prepared in the laboratory.
3. Precipitation experiments under the conditions cited indicate that Fe begins to precipitate at a pH of about 4.4 and that it is entirely precipitated at a pH of 5.0.
4. From the evidence presented, it is concluded that there is a critical pH at which a hardpan may be found in an acid clay soil and above which it cannot be formed.

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## RESIDUAL EFFECTS OF FORTY YEARS' CONTINUOUS MANURIAL TREATMENTS: II. EFFECT OF CAUSTIC LIME ON SOIL TREATED WITH BARNYARD MANURE

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In the first of the series of papers dealing with a detailed study of the plots treated with limestone and caustic lime (2) it was concluded (a) that there is no evidence to warrant the belief that caustic lime has a destructive action on soil organic matter in excess of such action by lime carbonates (b) that the excess of organic carbon found on the limestone treated soil as the result of earlier studies was derived from charcoal present in sufficient quantity to furnish 45.55 per cent of the total organic carbon found on the plot of tier 4.

### MANURE VERSUS LIME AND MANURE

Included in the various treatments of this old field experiment are plots to which are applied 6 tons of manure compared with an equal application of manure treated with 2 tons of raw burned lime. The manure in each case is applied biennially to the corn and wheat ground. The lime is applied once each 4 years to the land prepared for corn. The manure is applied on the clover sod for corn and on the oats stubble for wheat and is plowed under. The lime is applied after the ground is plowed and is then thoroughly harrowed into the seedbed. Prior to 1910, the lime was air-slaked and sometimes water-slaked before being spread. Since then raw ground lime has been used. From 1881 to 1921, 120 tons per acre of manure have been applied to each of plots 16 and 22. On plot 22, 20 tons per acre of lime have been added. These two plots form the basis for the present study together with additional studies on the two plots which have received applications of lime without manure. The manner of sampling, preparation of the soil for analysis, and chemical methods used are the same as previously reported (2, p. 209) except as otherwise stated. In this study each of the plots of the four tiers are separately analyzed including determinations of organic carbon, nitrogen, and alkali-soluble organic matter and nitrogen. The proportion of soil organic matter attributed to crop residues and to manure is estimated on the relation found to exist between the residual organic matter and the total yields of dry matter on similarly treated plots. The data secured as the result of earlier studies made on these plots are shown in table 1. In these studies, cited in the first paper (2), the samples from each tier of plots were combined as a unit. The 1921 data representing the

TABLE 1  
*Summary of the results secured on the 1899, 1911, 1915, and 1921*  
 Samples of the four tiers composited

PLOT NUMBER	PLOT TREATMENT	ORGANIC CARBON				NITROGEN			
		1899	1911	1915	1921	1899	1911	1915	1921
16	6 tons manure.....	per cent 1.89	per cent 1.961	per cent 2.042	per cent 1.968	per cent 0.1508	per cent 0.1523	per cent 0.1520	per cent 0.1533
22	Lime and 6 tons manure.....	1.79	1.869	1.908	1.855	0.1468	0.1589	0.1510	0.1569
Excess of organic matter on plot 16, pounds per acre*.....		3,400	3,172	4,620	3,867				

\* Computed on the basis of 2,000,000 pounds soil.

average composition of the four tiers of plots are also included in this table. These earlier studies, especially those of Hess, substantiated by the 1911 and 1915 data, are responsible for our misconceptions concerning the effect of lime on soil organic matter. Had each tier of plots been separately analyzed, the cause for the excess of organic matter on certain plots would no doubt have been discovered and would have led to an entirely different interpretation of the data.

#### EFFECT OF THE DISCOVERY OF CHARCOAL ON THE PLOTS

A more detailed study made since the publication of the first of the series of papers led to the discovery of charcoal on plots other than on tier 4. It becomes necessary, therefore, to examine each series of samples under consideration and to discard those that show more than a trace of charcoal. A careful examination of the plots of the four tiers included in the present study disclosed the presence of an appreciable amount of charcoal on plot 16 of tier 2. Unlike the condition found on several plots of tier 4, the charcoal appears to be distributed over the plot. Traces of charcoal were found on all the plots examined; however, the amount present would not seriously affect the organic carbon content of the soil. If the unscreened dry soil is shaken in a beaker with an excess of water the particles of charcoal will rise to the surface. In this manner each representative sample of soil is tested together with a careful examination of the soil in the field. An excess of charcoal will also widen the nitrogen-carbon ratio as shown in the case of plot 34, tier 4 (2, p. 208). On tier 2, plot 16, the ratio is 1:13.64 compared to 12.59 tier 1, 12.94 tier 3, and 11.37 tier 4.

In this section the land was heavily timbered, and when cleared a large proportion of the smaller timber was burned leaving behind a residue of charcoal. The presence of charcoal particles which are resistant to decay may be expected on all eastern soils, though little mention has been made of this fact. Reference to table 1 shows that when samples of the four tiers of plots are combined as a unit there is an excess of organic matter found on plot 16 (manure without lime). This difference in organic matter is due to charcoal found on plot 16 of tier 2. On tiers 1, 3 and 4 there is no significant difference in the organic matter content in excess of plot 22 (lime and manure). Based on the data of tables 3, 5, and 6, at least 25 per cent of the organic matter on plot 16, tier 2, is derived from charcoal. The fact that the difference in organic matter as shown in table 1 has remained fairly constant indicates that this excess is derived from a source resistant to decay.

Table 2 shows the average annual yield for the first 40 years of the experiment. With the exception of the first rotation the plot treated with lime and manure has given a greater yield throughout the 40 years. Lime has caused a total increased yield of 13,120 pounds dry matter including the following increased yields of the four crops: corn, 62 bushels; corn stover, 1080 pounds; oats, 16 bushels; oats straw, 2030 pounds; wheat, same yield; wheat straw, 10 pounds; and mixed hay, 4190 pounds.





DETAILED STUDY OF PLOT 16 (MANURE) AND PLOT 22 (LIME AND MANURE)  
OF EACH TIER OF PLOTS BASED ON THE 1921 SAMPLES (1881-1921)

The data secured as the result of a separate study of each tier of plots are shown in tables 3, 4, 5, 6, and summarized in table 7. With the exception of tier 2 there is no significant difference in the organic matter of the two manured

TABLE 3  
*Organic carbon and nitrogen found on plots of tier 1 (1881-1921)*

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
Organic carbon, per cent.....	2.231	2.188
Equivalent organic matter, pounds per acre*.....	76,925	75,442
Nitrogen, per cent.....	0.1783	0.1738
Nitrogen, pounds per acre.....	3,566	3,476
Nitrogen-carbon ratio.....	1:12.51	1:12.59

\* Organic carbon  $\times 1.724 \times 2,000,000$ .

TABLE 4  
*Organic carbon and nitrogen found on plots of tier 2 (1881-1921)*

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
Organic carbon, per cent.....	1.792	2.359*
Equivalent organic matter, pounds per acre.....	61,788	81,338
Nitrogen, per cent.....	0.1525	0.1730
Nitrogen, pounds per acre.....	3,050	3,460
Nitrogen-carbon ratio.....	1:11.75	1:13.64

\* Approximately 25 per cent charcoal carbon.

TABLE 5  
*Organic carbon and nitrogen found on plots of tier 3 (1881-1921)*

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
Organic carbon, per cent.....	1.644	1.679
Equivalent organic matter, pounds per acre.....	56,685	57,892
Nitrogen, per cent.....	0.1435	0.1298
Nitrogen, pounds per acre.....	2,870	2,596
Nitrogen-carbon ratio.....	1:11.45	1:12.94

plots. On an average of tiers 1, 3, and 4 the lime and manure treatment shows 1345 pounds of organic matter and 178 pounds nitrogen in excess of manure without lime. Expressed in equivalent percentages the difference is 0.039 per cent organic carbon and 0.0089 per cent nitrogen. We may conclude, therefore, that burned lime has not caused an excessive decomposition of organic matter as indicated by the earlier studies, but on the other hand the increased

yields due to lime have left in the soil a balance of organic matter derived from crop residue.

The increased yields on the lime-treated soil are due largely to more active azofication as shown by the fact that on each of tiers 1, 3, and 4, plot 22 contains an excess of nitrogen. The difference in nitrogen fixation is no doubt due to the fact that the soil treated with manure without lime is increasing in acidity as shown by frequent lime requirement determinations made during the progress of the experiment. In 1910 the Veitch lime requirement in pounds of  $\text{CaCO}_3$  per acre was 487; in 1915, 1695; and in 1921, 1830. A botanical analysis of the 1923 hay crop grown on tier 1 showed that there was a difference in

TABLE 6  
*Organic carbon and nitrogen found on plots of tier 4 (1881-1921)*

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
Organic carbon, per cent.....	1.755	1.647
Equivalent organic matter, pounds per acre.....	60,512	56,789
Nitrogen, per cent.....	0.1535	0.1448
Nitrogen, pounds per acre.....	3,070	2,896
Nitrogen-carbon ratio.....	1:11.43	1:11.37

TABLE 7  
*Summary of tables 3, 5, and 6 showing the average results secured on the plots of tiers 1, 3, and 4 (1881-1921)*

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
Organic carbon, per cent.....	1.877	1.838
Equivalent organic matter, pounds per acre.....	64,719	63,374
Nitrogen, per cent.....	0.1584	0.1495
Nitrogen, pounds per acre.....	3,168	2,990
Nitrogen-carbon ratio.....	1:11.85	1:12.29

the proportion of clover and timothy based on the two plots. The following data were secured:

TOTAL VEGETATION	PLOT 16	PLOT 22
	<i>per cent</i>	<i>per cent</i>
Red clover.....	22	51
Alsike clover.....	32	19
Timothy.....	43	24
Native weeds.....	3	6
Hydrogen-ion concentration.....	5.75	8.20
Lime requirement.....	2301	Alkaline

RELATIVE PROPORTIONS OF RESIDUAL ORGANIC MATTER AND NITROGEN  
ATTRIBUTED TO CROP RESIDUES AND TO APPLIED MANURE

There is no chemical method by which we may determine the origin of soil organic matter that exists in various stages of decay. For this reason no previous attempt has been made to determine the proportions of soil organic matter derived from crop residues and from applied manure. If, however, the total yields of dry matter produced per acre in 40 years is divided by the

TABLE 8

*Relative proportions of residual organic matter derived from manure and from crop residues per acre (average of tiers 1, 3, and 4)*

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
	<i>pounds</i>	<i>pounds</i>
Total yield of air-dry matter (1881-1921).....	185,640	172,520
Organic matter present in soil, 1921.....	64,719	63,374
Organic matter derived from crop residues*.....	60,077	55,832
Organic matter derived from manure (by difference)....	4,642	7,542
Total manure organic matter applied in 40 years.....	48,768	48,768
Manure organic matter decomposed in 40 years.....	44,126	41,226
Average annual decomposition of manure organic matter.....	1,103	1,031
Equivalent barnyard manure.....	5,428	5,071
Total organic matter present in excess of untreated soil.....	15,034	13,689
Increase in organic matter attributed to manure residue.....	4,642	7,542
Increase in organic matter attributed to crop residues...	10,392	6,147
Average annual gain in organic matter.....	376	342
Per cent of organic matter applied, decomposed in 40 years.....	90	84

\* Computed.

pounds per acre of residual organic matter found at the end of the same period. a fairly constant ratio is found to exist on similarly treated plots. Thus on the six highest yielding plots of the general fertilizer series treated biennially with complete fertilizers without lime, the following ratios were found to exist: 2.96, 3.01, 3.26, 2.98, 3.08, and 3.23—average 3.09. On the four manured plots which have received biennial applications of 6, 8 and 10 tons per acre of manure and 6 tons of manure with lime, the following ratios exist: 2.58, 2.62, 2.63, and 2.76, respectively—average 2.65.

The difference of 0.54 between the averages of each series is due to the presence of organic matter in the latter series in excess of that derived from crop residues.  $(3.09 - 2.65 \div 3.09 \times 100 = \text{per cent of total organic matter derived from manure.})$  Since the total yields in each series are similar the crop residues (roots and stubbles) left after harvest should be approximately the

same, especially on the same soil type. In other words, if the total yield of dry matter on each manure plot is divided by the normal factor 3.09 the proportionate crop residue organic matter will be determined. Thus the total organic matter of plots 22 and 16 (tiers 1, 3 and 4) is 64,719 and 63,374 pounds per acre respectively. The crop residue organic matter in the same order would be 60,077 and 55,832. The manure organic matter would by difference be 4642 and 7542 pounds per acre. The effect of lime is clearly shown by means of this comparison. Lime applied to the manured land has, according to the above figures, brought about the decomposition of 2900 pounds of manure organic matter in excess of manure without lime, resulting in sufficient increased yields (13,120 pounds dry matter) to cause an increase of 4245 pounds per acre of crop residue organic matter.<sup>1</sup> Table 8 shows the detailed data secured as the result of this study. The soil treated with lime and manure shows a loss of 90 per cent of the manure organic matter applied as compared to 84 per cent where manure was used without lime. On the lime and manure plot 93 per cent of the total organic matter found at the end of 40 years is derived from crop residues as compared to 83 per cent on the plot treated with manure without lime. If the manure organic matter found at the end of 40 years is computed in terms of original barnyard manure it will be seen that of the 120 tons applied, 11.4 tons were recovered on plot 22 and 18.5 tons on plot 16. The 20 tons of caustic lime applied to plot 22 has stimulated the decay of only 7.1 tons of manure above that attributed to normal decay as measured by the difference in organic matter between the two plots.

#### SOURCE OF NITROGEN ON MANURED PLOTS

The series of complete fertilizer plots which formed the basis for the organic matter studies show the following nitrogen-carbon ratios: 12.6, 12.4, 12.6, 12.3, 12.3, 12.3—average 12.4. If the organic carbon on the manured plots attributed to crop residues is divided by the normal factor 12.4 the proportion of total nitrogen derived from crop residues will be determined. Table 9 shows the data secured as the result of these computations. Plot 22 contains 198 more pounds of crop residue nitrogen and 20 pounds less manure nitrogen, or a balance of 178 pounds in excess of plot 16. However, 116 more pounds of nitrogen have been removed in crops from plot 22 than from plot 16; lime, has, therefore, caused an increase of 294 pounds of nitrogen excluding that lost by leaching.

#### RELATION OF YIELDS TO SOIL ORGANIC MATTER ON PLOTS TREATED WITH LIMESTONE AND WITH CAUSTIC LIME WITHOUT MANURE

It has been shown already that there exists a close relationship between the residual organic matter and the total yields of dry matter produced in 40 years

<sup>1</sup> The authors in using the terms "crop residue" and "manure organic matter" (later applied to nitrogen) do not mean to infer that there exists within the soil a distinctive chemical difference between the two forms of organic residue.

of continuous cropping. If we make the same study on a series of the lowest yielding plots including the untreated soil and those that have received single fertilizer ingredients such as nitrogen and potash without lime, it will be seen that a similar relationship exists; namely, untreated soil 2.07, nitrogen 2.05, and potash 2.08. These ratios show a closer relationship than exists on the high yielding plots. The high yielding plots show an average ratio of 3.09 compared

TABLE 9

*Relative proportions of nitrogen derived from manure and from crop residues per acre (average tiers 1, 3, and 4)*

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
	pounds	pounds
Total nitrogen present in soil, 1921.....	3,168	2,990
Nitrogen derived from crop residues*.....	2,810	2,612
Nitrogen derived from manure residues (by difference) ..	358	378
Nitrogen (from crop residues) in excess of untreated soil.....	550	350
Nitrogen removed in crops in excess of untreated soil†. .	792	676
Nitrogen applied in manure (1881-1921).....	1,200	1,200
Gain over untreated soil in excess of that applied.....	508	214
Gain in nitrogen on plot 22 in excess of plot 16.....	294	

\* Computed from N-C ratio.

† Not including nitrogen removed in legumes.

TABLE 10

*Effect of burned lime and limestone on soil organic matter*

Results expressed in pounds per acre

	PLOT 1-14 24-36 (UNTREATED)	PLOT 23 (BURNED LIME)	PLOT 34 (LIMESTONE)
Total yields of dry matter.....	103,400	114,320	123,880
Residual organic matter found in soil, 1921.....	49,168	51,070	49,983
Organic matter—yield ratio.....	2.07	2.20	2.46
Organic matter required to meet ratio.....		55,227	59,845
Organic matter decomposed (by difference).....		4,157	9,862
Nitrogen.....	2,188	2,324	2,344
Nitrogen removed in crops*.....	1,048	1,145	1,239
Nitrogen recovered in excess of untreated soil. . .		233	347

\* Not including nitrogen removed in legumes.

to 2.07 for the low yielding series. This difference is due to the fact that on the low yielding series a relatively larger percentage of the total weight of crops is left after harvest, since all plots regardless of the height of the plants are harvested in the same manner. The limestone and burned lime plots which have given similar yields show ratios of 2.46 and 2.20 respectively. On the two limed plots, therefore, there is less organic matter present in the soil in relation to the yields than is found on the untreated soil or those that have received single ingredients. If the yields of the two limed plots (23 and 34)

are divided by the normal ratio 2.07, the soil organic matter required to meet the normal organic matter yields ratio will be found; namely, 55,227 for burned lime and 59,845 for limestone. The actual pounds per acre of organic matter found on these two plots as previously reported (2, table 9) are 51,070 and 49,983 pounds respectively. The burned lime treated soil contains by difference 4157 pounds organic matter less than that required to meet the ratio as compared to 9862 pounds where limestone was used. Table 10 shows the data secured from this study. Limestone, based on these figures, has caused the decomposition of 5705 pounds per acre of organic matter in excess of burned lime. The limestone plot, however, as shown in table 10 has produced 114 pounds of nitrogen in excess of the burned lime plot. In other words, bacterial activity has been greater on the limestone plot. The difference in the effect of the two forms of lime is probably due to the variation in the actual amounts of active CaO applied. From 1881 to 1908, 89 per cent of the limestone used was coarser than 0.25 mm. After this, very fine material was used. A detailed study of the ultimate fate of the two forms of lime, as determined at the end of 40 years, shows that only 24 per cent of the total carbonates applied in the form of limestone had undergone decomposition from 1881 to 1921. It was determined also that only 13 per cent of the total CaO applied had been lost from the surface soil (data to be presented in the third of this series of papers) as compared to 39 per cent where burned lime was used. The burned lime was slaked before being applied, until 1910 after which ground raw burned lime was used. The excess of active CaO applied to the burned lime treated plot has no doubt retarded bacterial action at the same time the relatively small quantity of active CaO on the limestone treated soil has stimulated bacterial action, resulting in a greater decomposition of organic matter.

#### ORGANIC MATTER SOLUBLE IN 3 PER CENT SODIUM HYDROXIDE

It is of interest to study the ultimate effect of barnyard manure on the "humus" content of the limed and unlimed soils as compared to the untreated soil and those that have received lime without manure. It has already been shown that the total organic matter content of the manured plots is only slightly in excess of that attributed to crop residues. We may conclude, therefore, that the manure has maintained the organic matter of the soil indirectly by bringing about increased crop yields resulting in a greater accumulation of organic crop residues (93 per cent of the organic matter on plot 22, and 88 per cent on plot 16 are attributed to crop residues).

#### ANALYTICAL METHODS

Two methods were used to extract the alkali soluble humus: (a) by leaching on a Buchner funnel (b) by shaking soil with alkali on a Wagner shaking machine. The Buchner funnel, 4 inches in diameter, was provided with two



snugly fitting filter papers coated with a thin layer of fine asbestos. For a period of 3 hours 20-gm. portions of 1-mm. soil, ground to pass a 0.25-mm. screen, were washed with successive portions of 3 per cent NaOH. The alkali was allowed to percolate through the soil drop by drop. The first 150 cc. contained practically all the humus pigment. At the end of 3 hours the filtrate was removed from the filter flask and made up to a volume of 500 cc. Both the HCl-washed and original soil were extracted in this manner. The organic matter thus extracted may be considered as the easily soluble humus, or perhaps the true "matière noire" of Grandea. As will be shown, this readily soluble humus has the same nitrogen-carbon ratio as the original soil and differs somewhat from that extracted by prolonged shaking with the alkali in intimate contact with the soil.

TABLE 11

*Alkali soluble humus and proportion of total organic carbon and nitrogen present in the extracts, based on composite of tiers 1, 3, and 4*

Buchner funnel method

	PLOTS 1, 14, 24, 34 (UN- TREATED)	PLOT 23 (BURNED LIME)	PLOT 34 (LIME- STONE)	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)
	per cent	per cent	per cent	per cent	per cent
Alkali soluble humus, direct extraction (a)* . . . . .	0.8560	0.3550	0.3380	0.5540	1.1810
Alkali soluble humus, HCl washed soil (b)* . . . . .	1.0720	0.8890	0.9100	1.1450	1.4430
Humus carbon (a) . . . . .	0.4280	0.1770	0.1690	0.2770	0.5910
Humus carbon (b) . . . . .	0.5360	0.4450	0.4550	0.5730	0.7210
Humus nitrogen (a) . . . . .	0.0395	0.0225	0.0205	0.0280	0.0540
Humus nitrogen (b) . . . . .	0.0420	0.0345	0.0370	0.0495	0.0615
"Humate" carbon (b-a) . . . . .	0.1080	0.2680	0.2860	0.2960	0.1300
"Humate" nitrogen (b-a) . . . . .	0.0025	0.0120	0.0165	0.0215	0.0075
Non-humus carbon (total organic carbon—b) . . . . .	0.9050	0.9880	1.0350	1.3040	1.1170
Non-humus nitrogen (total nitrogen—b) . . . . .	0.0706	0.0806	0.0861	0.1089	0.0880
Total organic carbon soluble in NaOH (b) . . . . .	37.1900	31.0100	30.4900	30.5100	39.2400
Total nitrogen soluble in NaOH (b) . . . . .	37.3000	29.9700	30.0100	31.2500	41.1200
Nitrogen-Carbon Ratio (soil) . . . . .	12.79	12.45	12.09	11.85	12.29
Nitrogen-Carbon Ratio (humus—b) . . . . .	12.76	12.88	12.27	11.57	11.72
Nitrogen-Carbon Ratio (non-humus) . . . . .	12.81	12.26	12.03	11.99	12.69

\* Humus carbon  $\times 2$  = humus.

In the second method of humus extraction, 20-gm. portions of the HCl (1 per cent) washed soil were shaken with 500 cc. of 3 per cent NaOH for periods of 16, 40 and 88 hours. At the end of each period the respective flasks were set aside over night to allow the mineral matter to settle. The clear supernatant liquid was then transferred to a stoppered flask.

Both the humus carbon and nitrogen were determined in the alkali extract. The carbon was determined by oxidation in a boiling mixture of sulfuric and chromic acids according to the method proposed by White and Holben (3).



Corrections were made for the carbonate carbon contained in the original NaOH solution. Nitrogen was determined in the usual way by means of the Kjeldahl method.

Table 11 shows the data secured by extracting the humus on a Buchner funnel. The manured soil without lime shows, as would be expected, an excess of humus over the soil treated with lime and manure. It is of interest to note the slight difference between the humus content of the untreated soil and the soil treated with lime and manure. The three limed soils show a larger proportion of "insoluble humates." The nitrogen-carbon ratio comparison brings out the fact that the readily soluble humus has the same ratio as the soil and also the so-called non-humus material. If the advanced decay of soil organic matter is accompanied by a narrowing of the nitrogen-carbon ratio

TABLE 12

*Organic carbon and nitrogen extracted from the manured soils by shaking for different periods with 3 per cent NaOH, based on composite of tiers 1, 3, and 4*

	PLOT 22 (LIME AND MANURE)†			PLOT 16 (MANURE)†		
	Hours extracted			Hours extracted		
	16	40	88	16	40	88
	per cent	per cent	per cent	per cent	per cent	per cent
Alkali soluble humus*	1.500	1.858	2.1320	1.770	1.926	2.1320
Alkali soluble carbon	0.750	0.929	1.0660	0.885	0.963	1.0660
Alkali soluble nitrogen	0.073	0.086	0.1005	0.084	0.090	0.1005
Total organic carbon soluble in NaOH	39.950	49.500	56.8100	48.140	52.370	58.0100
Total nitrogen soluble in NaOH	46.090	54.290	63.4500	56.190	60.200	67.2300
Nitrogen-carbon ratio.....1:	10.27	10.81	10.61	10.53	10.69	10.61

\* Carbon  $\times 2$  = humus.

† Soil washed with HCl.

we may conclude that the humus thus extracted does not represent humified organic matter, if by humification we mean organic decay. These data seem to justify the conclusions of Gortner (1) who believes that specific humification of plant materials does not take place in soils, also that the humus extract of soils and plots is not a typical soil product, except in case of the black pigment included in the humus extract.

The amount of humus soluble in dilute alkali as shown in table 12 is dependent upon the length of time the extraction is continued. In case of the soil treated with lime and manure the total organic carbon soluble in 3 per cent NaOH varies from 30.51 per cent when leached for 3 hours on a Buchner funnel to 56.81 per cent when shaken for 88 hours on a Wagner machine. The nitrogen-carbon ratio of the several extractions indicates that continued contact of the soil with the alkali dissolves organic matter of the

same composition. These several extractions, however, show a nitrogen-carbon ratio which differs from the easily soluble organic material. The two manured soils show the same humus content where the extraction is continued for 88 hours. These data raise the question concerning the possible value of humus as a factor in soil fertility. The determination of the so-called "soil humus" appears similar to the estimation of water-soluble salts in that the amount dissolved depends upon the length of time the solvent is in contact with the soil mass or upon the number of subsequent extractions.

The European method of determining soil humus (organic carbon  $\times 1.724$ ) seems preferable to the alkali extraction method and serves as a better index of the productivity of the soil. Thus a soil treated with lime invariably shows less alkali-soluble organic matter than the same soil unlimed even though the total organic matter may be greater in the first case. The soil of plot 22 contains more organic carbon and nitrogen and less alkali-soluble organic matter than that of plot 16. The following comparison, in which the lime and manured soil is taken on a basis of 100, shows the relationship between the total and alkali soluble organic carbon and nitrogen and the yields of the several plots:

	PLOT 22 (LIME AND MANURE)	PLOT 16 (MANURE)	PLOT 23 (BURNED LIME)	PLOT 34 (LIME- STONE)	PLOTS 1, 14, 24 (UN- TREATED)
Yields (average dry matter).....	100	93	61	66	55
Total organic carbon .....	100	98	78	77	76
Total nitrogen.....	100	94	73	74	69
Humus carbon (Buchner funnel)....	100	126	77	89	93
Humus nitrogen (Buchner funnel)...	100	124	69	74	84
Humus carbon (16 hours extraction)...	100	118	68	74	83
Humus nitrogen (16 hours extraction).	100	115	72	72	79

The total nitrogen and organic carbon is shown to bear a closer relation to the yields than that soluble in dilute alkali, especially in case of the two manured soils. A more detailed study including a larger number of plots, however, is necessary before definite conclusions can be drawn. More detailed data on this subject will be reported in a later paper of this series.

#### SUMMARY

The following statements are based on a study of the two manured plots (numbers 16 and 22) at the end of 40 years of continuous treatment (1881-1921) during which time each plot has received 120 tons per acre of barnyard manure applied at the rate of 6 tons per acre to both the corn and wheat ground. Plot 22 in addition to manure has received during the 40 year period 20 tons per acre of burned lime applied at the rate of 2 tons per acre to the soil prepared for corn. The data presented are derived from a study of the condition and amount of soil organic matter with no reference to the mineral soil con-

stituents reserved for later study. The figures given are expressed on the acre basis (2,000,000 pounds) based on an average of tiers 1, 3, and 4.

1. The soil treated with lime and manure produced in 40 years 13,120 pounds of dry matter in excess of manure used without lime.

2. At the end of 40 years the lime and manure treated soil contained 64,719 pounds of organic matter and 3168 pounds of nitrogen compared to 63,374 and 2990 pounds, respectively, contained in the unlimed manured soil.

3. Lime applied to the manured soil has stimulated azofication, resulting in the fixation of 294 pounds of nitrogen in excess of the manure treatment without lime.

4. The lime and manure treatment showed a gain of 508 pounds of nitrogen in excess of the untreated soil compared with 214 pounds when manure was used alone.

5. Each of the manured plots has received in 40 years 48,768 pounds per acre of manure organic matter of which 90 per cent has been decomposed on the lime and manure plot and 84 per cent where manure was used without lime (computed from the yields—organic matter ratio explained in the text).<sup>1</sup>

6. It is estimated that 93 per cent of the organic matter of the lime and manure plot is derived from crop residues compared to 88 per cent on the plot treated with manure alone.

7. Manure has decomposed at an average annual rate of 5428 pounds per acre where lime was applied, compared to 5071 pounds where used alone.

8. The lime and manure plot contained 15,034 pounds of organic matter in excess of the untreated soil of which 4642 pounds are attributed to manure residue and 10,392 pounds to accumulated crop residues.

9. The unlimed manure plot contained 13,689 pounds of organic matter in excess of the untreated soil of which 7542 pounds are attributed to manure residue and 6147 pounds to accumulated crop residues.

10. Lime applied to the manured land has stimulated the decay of 2900 pounds of organic matter in excess of the manure treatment without lime, resulting in sufficient increased yields of crops to cause an accumulation of 4245 pounds of organic crop residues, leaving a balance of 1345 pounds of organic matter in excess of the manure treatment without lime.

11. The excess of organic matter found on the unlimed manured plot as the result of earlier studies (1899–1900, 1911 and 1915) was found to be due to the presence of charcoal on plot 16 of tier 2. On this plot approximately 25 per cent of the organic carbon is derived from charcoal residues. (Table 4.)

12. The manured soil treated with lime contained less readily soluble humus (Buchner funnel method) than the unlimed manured soil.

13. When the two soils were shaken for 88 hours with 3 per cent NaOH the same percentage of humus carbon and nitrogen was extracted.

14. The organic carbon or nitrogen content of a soil is shown to be a better index of productivity than the alkali-soluble humus.

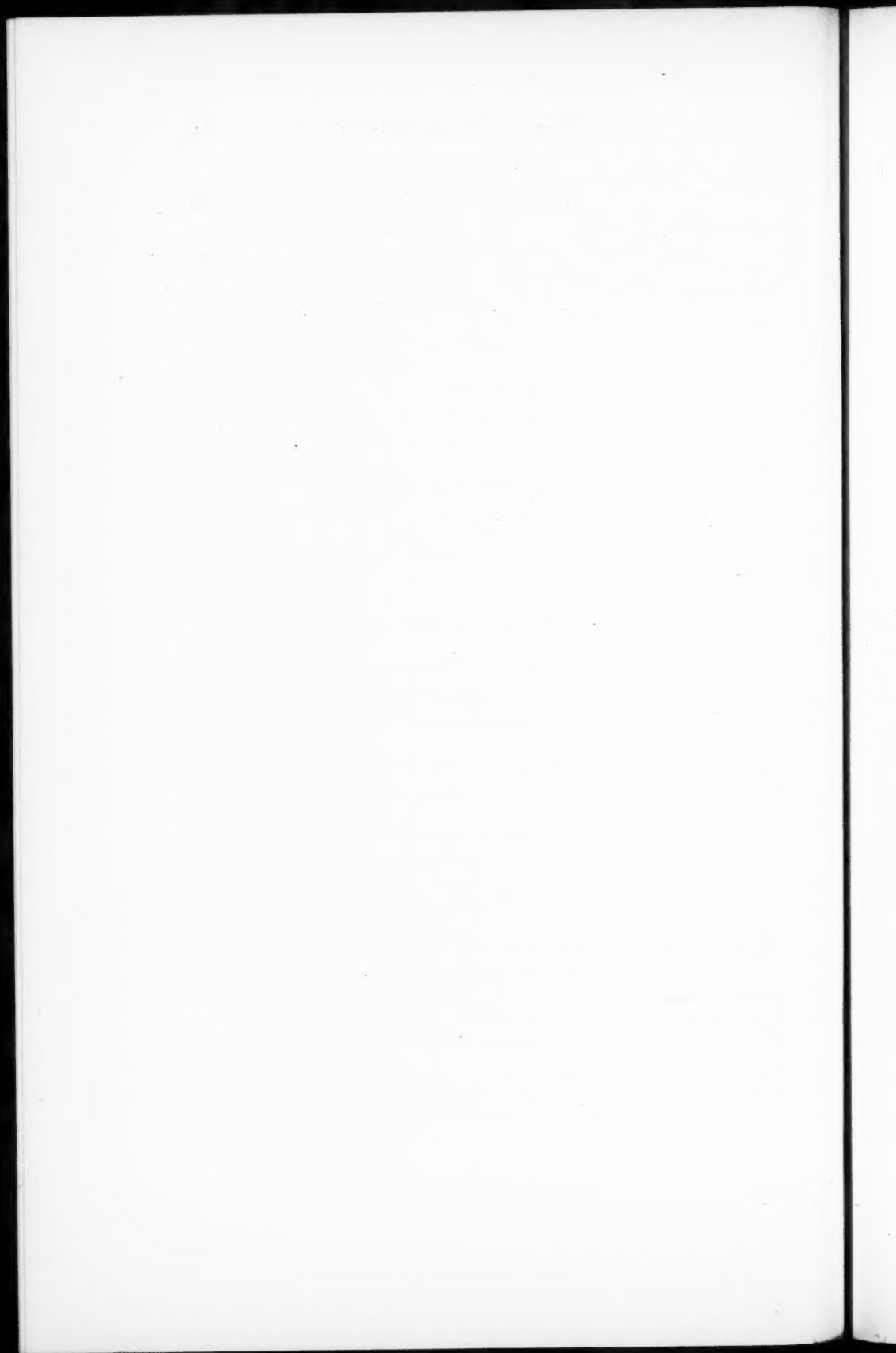
15. The proportion of soil organic matter soluble in dilute alkali is dependent upon the length of time the extraction is continued. It has been shown to vary from 30.51 to 56.81 per cent. (Lime and manure soil, tables 11 and 12.)

16. The alkali-soluble organic matter determined by leaching the soil in a Buchner funnel with 3 per cent NaOH shows the same nitrogen-carbon ratio as the total soil organic matter. The humus extracted by prolonged shaking shows a different ratio from the easily soluble humus.

17. The data gained from a study of the alkali-soluble organic matter of the several plots indicate that the so-called "soil humus" is not a definite soil material which may be completely extracted from a soil to the exclusion of the "unhumified" organic matter.

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# THE INFLUENCE OF THE AMOUNT AND NATURE OF THE REPLACEABLE BASE UPON THE HEAT OF WETTING OF SOILS AND SOIL COLLOIDS<sup>1</sup>

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The colloidal content exerts a very marked influence upon the heat of wetting of the soil. Anderson (1) and Bouyoucos (2) have suggested the ratio

$$\frac{\text{heat of wetting per gram of soil}}{\text{heat of wetting per gram of colloid}} \times 100$$

as a method of estimating the percentage of colloid contained in a soil. In determining the heat of wetting of colloids both investigators found that the colloids extracted from different soils had different heats of wetting, but no satisfactory explanation for this difference was given. It must be caused by a difference in chemical or physical nature of the colloids or by both. Bouyoucos says that it is caused by a difference in both physical and chemical nature but that the physical nature of the surface of the colloidal particle is probably the most important factor. If this is true it would be reasonable to suppose that the nature of the replaceable base would exert an influence, because it is well known that the physical properties of soils are largely influenced by the nature of the replaceable base. Gedroiz (4, p. 37) has shown that monovalent bases, especially sodium, have a tremendous deflocculating effect upon a soil, whereas divalent and trivalent bases have a strong flocculating effect. If the soil structure is affected so much by the nature of the replaceable base it is apparent that the nature of the colloid would likewise be affected, since the replaceable base is found chiefly in the colloidal fraction. Of course the chemical composition is changed by a change of replaceable base but this may be relatively unimportant as compared to the physical change brought about.

Since the heat of wetting of soils is dependent upon the nature of the colloid present as well as upon the quantity, as shown by Anderson (1) and Bouyoucos (2), it was thought that saturating a soil with different bases and thereby changing the physical nature would produce a change in the heat of wetting. The present work was planned with this idea in mind. It was soon evident that a similar study of extracted colloid would be of interest; accordingly a study was made of colloids extracted from some of the soils studied.

<sup>1</sup> The writer wishes to express his appreciation for the helpful suggestions and criticism tendered by Dr. F. W. Parker during the course of the investigation.

## EXPERIMENTAL

The soils used in this investigation vary widely in type, content of replaceable base, and colloid content, as may be seen from table 1. The colloid content was calculated on the adsorption ratio of Robinson (10) while the replaceable base content was determined by a method similar to that of Kelley and Brown (9). The colloid content varied from 9.99 per cent in the Norfolk sandy loam to 63.3 per cent in the Oktibbeha clay. The replaceable base content had even a greater variation. The Norfolk sandy loam contained only 1.67 mgm. equivalents of replaceable base per 100 gm. of soil whereas Oktibbeha clay had 30.8 mgm. equivalents. However, when these soils are arranged in the order of their colloid content they are also in the order of their replaceable base content. This indicates that most or all of the replaceable base would

TABLE 1  
*Colloid and replaceable base content of soils used*

SOIL TYPE	COLLOID CONTENT	REPLACEABLE BASE*	COLLOID REPLACEABLE BASE
	<i>per cent</i>	<i>mgm. eq.</i>	
Norfolk sandy loam.....	9.99	1.67	5.97
Clarksville silt loam.....	10.60	2.74	3.87
Holston silt loam.....	17.43	3.27	5.34
Greenville sandy loam.....	16.40	3.46	4.74
Hollywood clay loam.....	22.70	19.88	1.14
Oktibbeha clay.....	63.30	30.80	2.05

\* Milligram equivalents based on 100 gm. of soil and calculated according to the method of Kelley and Brown (9).

be found in the colloidal portion of the soil. The last column of the table gives the  $\frac{\text{colloid}}{\text{replaceable base}}$  ratio. This varies considerably, indicating that different colloids may contain widely different amounts of replaceable base.

*Experiment 1*

The purpose of this experiment was to determine the heat of wetting of several soils when saturated with different bases. They were saturated with Na, K,  $\text{NH}_4$ , Ba, Ca, and Mg by a procedure similar to that of Kelley and Brown (9) by using normal solutions of the chlorides. After saturation the samples were washed free from chlorides and dried overnight in an oven at  $110^\circ\text{C}$ . At the same time samples were saturated with H by using 0.05 *N* HCl and an untreated sample was leached with distilled water and subjected to the same drying process as the other samples. The heat of wetting of all samples was determined by a method similar to that of Bouyoucos (2) with the exception that a constant temperature water bath was used to keep the soils and calorimeter at a constant temperature.



The results of heat of wetting determinations are given in table 2. It is readily seen from this table that there is a great difference in the amount of heat given off by a soil when saturated with different bases. The results for Norfolk sandy loam are subject to considerable error because of the extremely low heat of wetting. However, the results for the other soils are generally consistent and conclusive. In general the soils have a low heat of wetting when saturated with monovalent bases. The greatest variation is found in the Oktibbeha clay. The sample saturated with potassium gave a heat of wetting of 6.27 calories per gram whereas the untreated sample gave a heat of wetting of 11.66 calories per gram. This is a decrease of 46 per cent. It will be seen that in all cases except one, the heat of wetting was decreased by monovalent bases. Very probably some of this decrease is accounted for by a loss of organic matter during the leaching process. Without exception, when the chlorides from the samples saturated with Na, K, and  $\text{NH}_4$  were washed, a black leachate

TABLE 2  
*Heat of wetting, in calories per gram, of soils saturated with different bases*

BASE	NORFOLK	CLARKSVILLE	HOLSTON	GREENVILLE	HOLLYWOOD	OKTIBBEHA
	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>
Na.....	0.55	0.98	1.59	1.74	4.99	8.12
K.....	0.51	0.84	1.34	1.77	3.66	6.27
$\text{NH}_4$ .....	0.58	0.80	1.27	1.58	3.76	7.25
Ba.....	0.54	0.89	1.56	1.78	5.54	10.48
Ca.....	0.60	1.04	1.61	1.85	6.64	11.08
Mg.....	0.49	1.01	1.44	1.76	6.70	11.11
H.....	0.52	0.89	1.15	1.67	4.85	10.43
Untreated.....	0.69	1.03	1.45	1.96	6.10	11.66

was obtained indicating a solubility of organic matter. However, this loss was not great because, as the coloration indicated practical freedom from chlorides, the washing was discontinued.

On the whole the divalent bases did not exert a marked influence upon the heat of wetting of the soil. In a few instances there was an increase, although in most instances the result was a slight decrease when compared with the untreated sample. These results are in agreement with what might be expected from a study of the replaceable base content of soils. Hissink (6), Gedroiz (4, 5) and Kelley and Brown (9) have found that for the average soil 80 to 90 per cent of the replaceable bases are divalent. The change brought about by saturation with divalent bases is, therefore smaller than that caused by saturation with monovalent bases.

From the table it may be seen also that the greatest change was produced in those soils containing high percentages of colloidal material. This indicates that most of the replaceable base is in the colloid. That being the case, it would be of interest to determine the heat of wetting of extracted colloid after saturating it with different bases. This was done in experiment 2.

*Experiment 2*

The colloids were extracted by methods similar to those used by Bradfield (3) and the Bureau of Soils (11). Twenty-gram samples were then saturated with different bases by washing, by decantation with normal solutions of the respective chlorides. After saturation the samples were washed free of chlorides by decantation. Samples saturated with ammonium and calcium were prepared. The heat of wetting was determined on these and on untreated samples. The results are given in table 3, from which it may be seen that the replaceable base may exert a very marked influence upon the heat of wetting of a colloid. In every instance the samples saturated with calcium had a higher heat of wetting than the untreated samples or those treated with ammonium. The greatest difference between ammonium and calcium treated samples occurred in the colloid from Oktibbeha clay. In this colloid the sample saturated with ammonium gave practically 60 per cent as great heat of wetting as the sample saturated with calcium. The differences between the mono- and

TABLE 3  
*Heat of wetting, in calories per gram, of soil colloids saturated with different bases*

BASE	HOLSTON	CLARKSVILLE	OKTIBBEHA	HOLLYWOOD	SUSQUE- HANNA
	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>
NH <sub>4</sub> .....	6.50	6.92	9.69	8.86	10.24
Ca.....	.....	8.72	16.06	13.43	16.34
Untreated.....	7.34	8.31	11.49	11.77	14.40

divalent bases and the untreated sample are not constant. Probably the results for monovalent bases in colloids are more nearly correct than for monovalent bases in soils, for the solubility of organic matter was not evidenced by the black leachate in the case of colloids.

A comparison of the results for the different colloids show that the Holston and Clarksville colloids differ from the other three in their behavior. In the first place the colloids from Holston and Clarksville soils have a much lower heat of wetting than any of the others. In the second place the nature of the replaceable base does not change the heat of wetting as much as in the other samples of colloid. Since the nature of the replaceable base influences the heat of wetting it seems possible that the small influence of the nature of the replaceable base on the heat of wetting of Holston and Clarksville colloids may be due to a low content of replaceable base. The low content of replaceable base may be one factor causing the low heat of wetting of the colloid. The replaceable base content of these colloids was determined, with the results given in table 4.

The results show that there is a good correlation between the heat of wetting and the replaceable base content of the colloid. The correlation would be better if the comparison were made using the heat of wetting of the ammonium or

calcium saturated samples. The untreated colloid varies in the nature of the replaceable base which causes some variation in the heat of wetting.

If there is a good positive correlation between the heat of wetting of colloids and their replaceable base content it seems probable that both of these properties would be related to the chemical composition of the colloid. Joseph (8) has shown a close correlation between  $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$  ratio and the moisture equivalent.

TABLE 4  
*Relation of heat of wetting to the content of replaceable base in colloids from different soils*

SOIL	HEAT OF WETTING	REPLACEABLE BASE*	REPLACEABLE BASE DIVIDED BY HEAT OF WETTING
	cal.	mgm. eq.	
Holston colloid . . . . .	7.34	10.65	1.45
Clarksville colloid . . . . .	8.31	18.32	2.20
Oktibbeha colloid . . . . .	11.49	50.20	4.36
Hollywood colloid . . . . .	11.77	37.27	3.16
Susquehanna colloid . . . . .	14.40	44.87	3.11

\* Milligram equivalents based on 100 gm. of colloid and calculated according to the method of Kelley and Brown (9).

TABLE 5  
*Relation of chemical composition to the heat of wetting, dye absorption, and ammonia absorption by colloids from different soils*

SOURCE OF COLLOID	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	HEAT OF WETTING	DYE ABSORPTION	AMMONIA ABSORPTION	WATER ABSORPTION
		cal.	per cent	per cent	per cent
Cecil clay subsoil . . . . .	1.20	4.5	15.82	1.92	28.70
Chester loam soil . . . . .	1.77	7.2	13.48	2.93	23.98
Norfolk fine sandy loam subsoil . . . . .	1.84	6.0	11.58	2.95	27.55
Sassafras silt loam subsoil . . . . .	1.89	9.8	21.88	3.40	30.97
Miami silt clay loam subsoil . . . . .	2.66	11.8	20.96	3.58	30.75
Marshall silt loam soil . . . . .	2.82	14.2	29.78	5.36	29.40
Sharkey clay soil . . . . .	3.07	16.3	37.57	6.09	30.80
Wabash silt loam soil . . . . .	3.16	17.6	36.98	6.14	33.25

Bouyoucos (2) states that he failed to find a correlation between chemical composition and the heat of wetting but he does not give the analysis of the colloids studied. Anderson (1) determined the heat of wetting of colloids whose chemical composition and absorptive properties had been determined by Robinson (11), Gile et al. (6). Anderson apparently did not make a study to determine whether the heat of wetting was correlated with the chemical composition or absorptive properties of the colloids. The author, however, has made such a study, the data of which are presented in table 5. The colloids are those studied by Anderson. All results are taken from the Bureau of Soils publi-

cations (1), (6) and (11). The soils are arranged in the order of their  $\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$  ratio.

The data show that there is an excellent correlation between the chemical composition (as indicated by the  $\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$  ratio), the heat of wetting, and the absorption of ammonia and dye by the colloid. Unfortunately, the replaceable base content of these colloids is not known but it is very probable that it would correlate well with the chemical composition. There is little or no correlation between the chemical composition and the water absorption of soil colloids.

The relation of the heat of wetting to the chemical composition and replaceable base content of colloids is being investigated further at this laboratory.

#### SUMMARY

The influence of the nature of the replaceable base on the heat of wetting of soils was studied by saturating soils with different bases and determining the heat of wetting. A similar study was made with colloid extracted from some of the soils. In all cases the soil or colloid saturated with a monovalent base gave a lower heat of wetting than the soil or colloid saturated with a divalent base.

The extracted colloid from different soils gave different heats of wetting and contained different amounts of total replaceable base. The colloid with a high replaceable base content gave a high heat of wetting, whereas the colloid with a low replaceable base content gave a low heat of wetting. Apparently the amount of replaceable base is an important factor determining the heat of wetting of soil colloids.

A study of the data from the Bureau of Soils (1), (6), (11) shows that there is a good correlation between the chemical composition of soil colloid, its heat of wetting, and the amount of ammonia and dye it will absorb. Colloids having a high  $\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$  ratio have a high heat of wetting and absorb large amounts of ammonia and dye. Colloids having a low  $\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$  ratio have a low heat of wetting and absorb small amounts of ammonia and dye.

It is probable that there is a good correlation between the  $\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$  ratio of soil colloids and their content of replaceable base. This problem is being studied.<sup>2</sup>

<sup>2</sup> Since this paper was submitted for publication several articles have been published that have a direct bearing on certain phases of this investigation. The more important articles are:

1. Bouyoucos, G. J. 1925 The chief factors which influence the heat of wetting of soil colloids. *In Soil Sci.*, v. 19, p. 477-482.
2. Joseph, A. F. 1925 Clay as soil colloids. *In Soil Sci.*, v. 20, p. 89-94.
3. Anderson, M. S. and Mattson, S. E. 1925 The relation between properties and chemical composition of soil colloids. *In Science*, v. 62, p. 114-115.

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- (3) BRADFIELD, R. 1923. The chemical nature of a colloidal clay. *Mo. Agr. Exp. Sta. Res. Bul.* 60.
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- (6) GILE, P. L., MIDDLETON, H. E., ROBINSON, W. O., FRY, W. H., AND ANDERSON, M. S. 1924 Estimation of colloidal material in soils by adsorption. *U. S. Dept. Agr. Bul.* 1193.
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